

LOGARITHMS

②

Number	0	1	2	3	4	5	6	7	8	9	123	456	789
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	122	345	557
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	122	345	567
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	122	345	567
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	112	344	567
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	112	344	567
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	112	344	566
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	112	344	566
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	112	334	566
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	112	334	556
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	112	334	556
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	112	334	556
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	112	334	556
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	112	334	556
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	112	334	456
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	112	234	456
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	112	234	456
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	112	234	455
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	112	234	455
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	112	234	455
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	112	234	455
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	112	233	455
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	112	233	455
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	112	233	445
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	112	233	446
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	112	223	445
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	112	233	445
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	112	233	445
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	112	233	445
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	112	233	445
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	112	233	445
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	112	233	445
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	112	233	445
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	011	223	344
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	011	223	344
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	011	223	344
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	011	223	344
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	011	223	344
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	011	223	344
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	011	223	344
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	011	223	344
95	9777	9782	9786	9791	9795	9800	9805	9810	9814	9818	011	223	344
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	011	223	344
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	011	223	344
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	011	223	344
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	011	223	334
	0	1	2	3	4	5	6	7	8	9	123	456	789

LOGARITHMS

Number	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4 8 12	17 21 25	29 33 37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4 8 11	15 19 23	26 30 34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3 7 10	14 17 21	24 28 31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3 6 10	13 16 19	23 26 29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3 6 9	12 15 18	21 24 27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3 6 8	11 14 17	20 22 25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3 5 8	11 13 16	18 21 24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2 5 7	10 12 15	17 20 22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2 5 7	9 12 14	16 19 21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2 4 7	9 11 13	16 18 20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2 4 6	8 11 13	15 17 19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2 4 6	8 10 12	14 16 18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2 4 6	8 10 12	14 15 17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2 4 6	7 9 11	13 15 17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2 4 5	7 9 11	12 14 16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2 3 5	7 9 10	12 14 15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2 3 5	7 8 10	11 13 15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2 3 5	6 8 9	11 13 14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2 3 5	6 8 9	11 12 14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1 3 4	6 7 9	10 12 13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1 3 4	6 7 9	10 11 13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1 3 4	6 7 8	10 11 12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1 3 4	5 7 8	9 11 12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1 3 4	5 6 8	9 10 12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1 3 4	5 6 8	9 10 11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1 2 4	5 6 7	9 10 11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1 2 4	5 6 7	8 10 11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1 2 3	5 6 7	8 9 10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1 2 3	5 6 7	8 9 10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1 2 3	4 5 7	8 9 10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1 2 3	4 5 6	8 9 10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1 2 3	4 5 6	7 8 9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1 2 3	4 5 6	7 8 9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1 2 3	4 5 6	7 8 9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1 2 3	4 5 6	7 8 9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1 2 3	4 5 6	7 8 9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1 2 3	4 5 6	7 7 8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1 2 3	4 5 5	6 7 8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1 2 3	4 4 5	6 7 8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1 2 3	4 4 5	6 7 8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1 2 3	3 4 5	6 7 8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1 2 3	3 4 5	6 7 8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1 2 2	3 4 5	6 7 7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1 2 2	3 4 5	6 6 7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1 2 2	3 4 5	6 6 7
	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9

GOVT. COLLEGE FOR WOMEN SRINAGAR
LIBRARY
—o—

Class No. 540.2

Book No. k 52 c

Acc. No. 840

Al. 12 Sc HCH
337 53
— ©

CHEMICAL CALCULATIONS

Practical Chemistry
by
Hashmi &
Suman

by J. A. Mitchell
QUANTITATIVE CHEMISTRY

by J. A. Mitchell and C. W. Hyde
SYSTEMATIC CHEMICAL CALCULATIONS

cat

②

CHEMICAL CALCULATIONS

Their Theory and Practice

A. KING

M.Sc., A.R.C.S., D.I.C.

*Lecturer in Physical and Inorganic Chemistry
Imperial College of Science and Technology*

AND

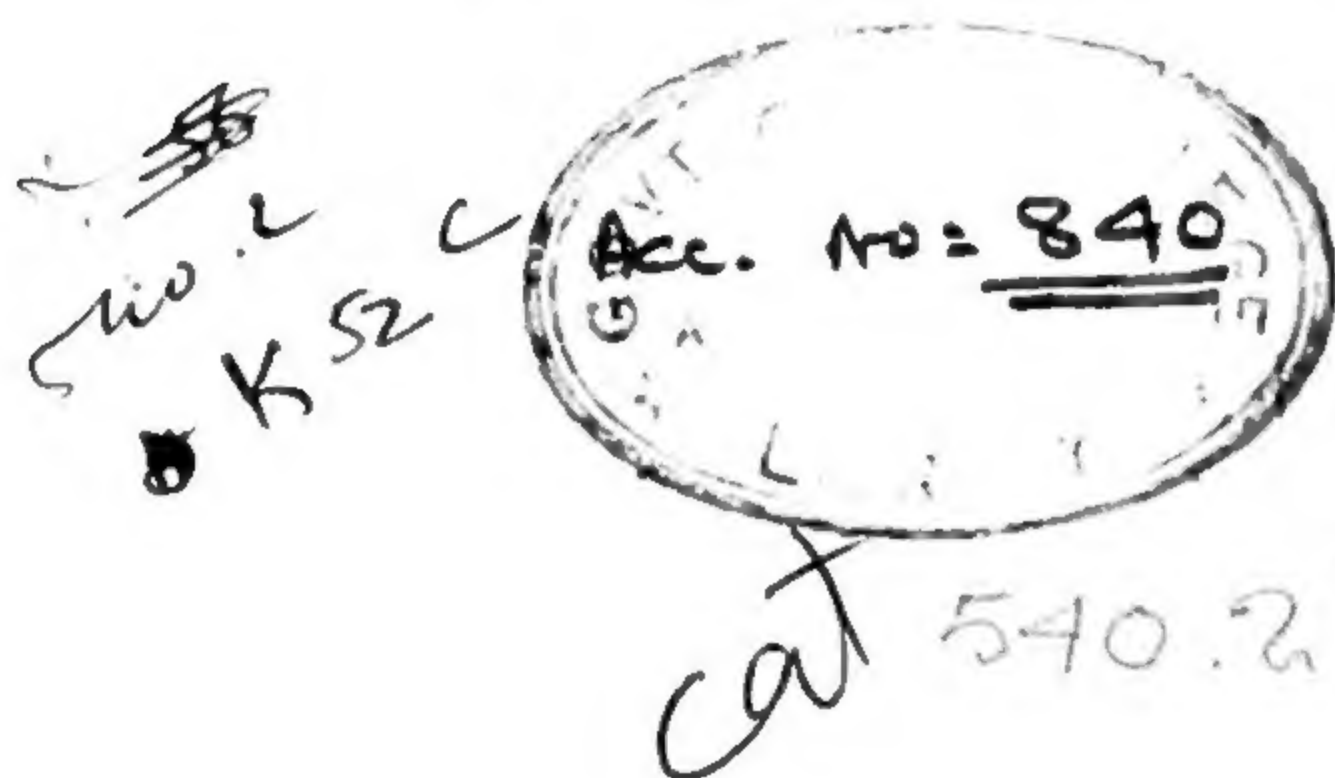
J. S. ANDERSON

PH.D., A.R.C.S., D.I.C.

*Senior Lecturer, Chemistry Department
University of Melbourne*

LONDON
GEORGE ALLEN & UNWIN LTD

First Published, November, 1933.
Second Edition, Revised, with additional
Examples, June, 1939.
Reprinted, 1945, 1947 and 1948.



540.2

K534

PRINTED IN GREAT BRITAIN
BY
THE WOODBRIDGE PRESS, LTD., GUILDFORD.

INTRODUCTION

BY PROFESSOR H. V. A. BRISCOE, D.Sc.

It is a pleasure to commend this little book to those who study chemistry or who are responsible for its teaching.

The acquisition of a reasonable facility in chemical calculations is important not merely for utilitarian reasons—though these are strong enough—but chiefly because it is the readiest and surest way to gain a grip upon the fundamental theory and science of chemistry. Hence it is a special merit of this book that the discussion and illustration of each type of calculation is accompanied by a brief, but clear and sufficient, exposition of the relevant points of principle.

The authors' experience as teachers, especially of undergraduate classes, has enabled them to see and appreciate the difficulties commonly encountered by the student, and also to select or devise methods calculated to avoid or surmount those difficulties. Therefore the book should prove valuable, in my opinion, both to the teacher and to the student who works alone. An ingenious and simple device, new to me, makes the book usable in both ways, since both those who want and those who do not want answers are provided for, respectively, by the odd- and even-numbered examples.

Many of us must feel grateful to the authors for their labours in giving us such a considerable body of new and interesting problems, doubly valuable because they are

■

set upon a background of sound philosophy, and the book should be specially helpful to the many students of chemistry who work without much guidance or help from teachers. They may, I feel, have every confidence that here they may find a very trustworthy guide and mentor.

IMPERIAL COLLEGE OF
SCIENCE AND TECHNOLOGY.

September, 1933.

b

PREFACE

The working of chemical calculations has long been recognised as a means of familiarising the student with the fundamental laws of chemistry. It is often found, however, that the elementary student does not grasp the connection between such calculations and the theoretical principles on which they are based, and which he can only find scattered amongst the descriptive matter in his general text-books. The present book sets out to discuss adequately, if briefly, the elementary laws and theories of chemistry, making application at every stage to calculations. In so far, therefore, as its scope differs somewhat from the majority of text-books of chemical calculations published hitherto, the authors make no apologies for its appearance. It in no way seeks to replace the general text-books, but rather to supplement them by collecting together the theoretical matter they contain, and presenting it in close proximity to the calculations.

Although the sequence in which the matter is presented is as logical as possible, a certain use of normalities has had to be introduced into chapter V in connection with electrochemical measurements, before the subject has been discussed in chapter VI. It will probably be found convenient to introduce the more elementary calculations of volumetric analysis earlier in the course, without discussing the ionic hypothesis as fully as is done in chapter V.

The attention of both student and teacher is drawn to the numerous references to important pieces of original work which appear in the text. The student cannot too early acquire the habit of reading for himself the classical experimental work which forms the foundation of the theory.

The book roughly covers that part of the subject in the syllabus of the Intermediate Science examination of the University of London and the Higher Schools Certi-

ficate, although the earlier parts are suitable for Matriculation candidates. It is thus generally intended for first year students in the Universities and for the higher classes in schools.

The actual methods of calculation illustrated in the text are as simple and short as possible, while seeking to eradicate "substitution in formulæ." The examples on the use of the gram-molecular volume illustrate the stress that has been laid on the use of straightforward calculation. In the chapter on volumetric analysis, calculations are in all cases worked out by the rational use of normalities, and the student should have no difficulty in applying the principles to the working out of volumetric results of any kind.

500 new and graded problems have been composed or adapted from original experimental work for this book. The presence of a complete list of answers in a book of this sort is often an embarrassment to the teacher, but is yet extremely useful to the student preparing for examinations by private study. To meet these two needs as far as possible, answers are throughout given to alternate problems.

Finally, the position of the logarithm tables on the inside boards at the beginning, and of the antilogarithms at the end, of the book is intended to save the time and preserve the patience of the student. For the same reason, the logarithms of certain numbers frequently recurring in chemical problems are given a certain prominence.

September, 1933.

A. KING,
J. S. ANDERSON.

NOTE TO SECOND EDITION

We desire to thank the University of London for permission to reprint from their intermediate examination papers, examples 506 to 530, which have been added to the present edition.

CONTENTS

	PAGE
INTRODUCTION BY PROFESSOR H. V. A. BRISCOE, D.Sc.	v
PREFACE	vii

CHAPTER I

THE LAWS OF COMBINATION. EQUIVALENTS ...	1
Conservation of Mass. Work of Stas, Morley and Landolt. Law of constant proportions. Law of multiple proportions. Chemical equivalents. Determination of equivalents	

CHAPTER II

THE ATOMIC THEORY	20
The atomic structure of matter. Laws of combination and the atomic theory. Difficulties of the atomic theory. Modern theory of the structure of matter. Formulæ. Formulæ from percentage composition. Equations. Gravimetric analysis	

CHAPTER III

THE MOLECULE AND MOLECULAR WEIGHT	38
Law of gas volumes. Avogadro's hypothesis. Calculations involving gas volumes. Gas analysis calculations. Molecular weight and molecular volume. Gas and vapour densities. Dissociation and association. Diffusion	

CONTENTS

CHAPTER IV

	PAGE
ATOMIC WEIGHTS	73
Atomic weight, equivalent and valency. Cannizzaro's method. Dulong and Petit's rule. Isomorphism. The accurate determination of atomic weights. Inter-relation of the atomic weights	

CHAPTER V

ELECTROLYSIS AND THE IONIC THEORY. MOLECULAR WEIGHT OF DISSOLVED SUBSTANCES ...	90
Electrolysis. Faraday's laws. Ionic hypothesis. Conductivity of electrolytes. Osmotic pressure. Molecular weight from osmotic pressure. Molecular weight from freezing point depression and from boiling point elevation	

CHAPTER VI

VOLUMETRIC ANALYSIS	110
The equivalent weights of compounds. Normalities. Acids and bases. Indicators. Acid-alkali titrations. Titrations involving oxidation. Iodine titrations. Precipitation analyses. Miscellaneous calculations	

CHAPTER VII

THERMOCHEMISTRY	149
Energy in chemical reactions. The conservation of energy. The law of Hess. Indirect calculation of heats of reaction	
MISCELLANEOUS PROBLEMS	164
ANSWERS TO PROBLEMS	175
TABLE I—ATOMIC WEIGHTS	179
TABLE II—TENSION OF WATER VAPOUR	180
INDEX	181

CHAPTER I

THE LAWS OF COMBINATION. EQUIVALENTS

The quantitative study of chemical combination has led to the formulation of the natural laws, subject to which chemical change occurs; viz., the law of the conservation of mass, the laws of constant and of multiple proportions, and the law of equivalent proportions or combining weights.

THE CONSERVATION OF MASS

The first of these laws, the law of the conservation of mass is, indeed, a tacit assumption which underlies the whole of chemistry as a quantitative science. The law may be stated: in the course of any chemical reaction, matter is neither created nor annihilated; the mass of the substances reacting is equal to the mass of the products formed by the reaction: *i.e.*, if any reaction be considered, such as



then, the weight of $(A + B)$ = the weight of $(C + D)$.

The truth of the law of the conservation of matter had been assumed, tacitly or explicitly, by many investigators and philosophers, from the time of Democritus onwards. The imponderability of heat, however, and the acknowledgment of weight or mass as the fundamental and distinguishing characteristic of matter were not fully recognised until the latter half of the eighteenth century, and it was only then that the law of conservation of mass, really implicit in the axiom of the conservation of matter, was formally stated. It was left to Lavoisier, as part of

his work which overthrew the phlogiston theory, to demonstrate the truth of the law and to gain for it universal acceptance.

Lavoisier showed that if a chemical change, *e.g.*, the calcination of tin, were carried out in a closed vessel, which was weighed before and after the reaction, no change in weight occurred;

i.e., Weight of tin + Weight of air = Weight of tin oxide
+ Weight of residual air.

Further, he showed that when other metals—mercury and iron—were converted to their oxides, invariably, within the experimental error,

Weight of metal + weight of oxygen absorbed = weight
of oxide formed.

Although the experiments of Lavoisier were not very accurate, they served to demonstrate the essential truth of the conservation of mass.

THE WORK OF STAS

The truth of the law has been thereafter always assumed, any discrepancy between weight of reactants and weight of products being ascribed to experimental error. Thus Stas, in his very accurate researches on combining weights, carried out a number of complete analyses and syntheses, with a view to using the difference between the weight of the reactants and the weight of the products as a direct measure of the accuracy of the work. His data may, however, well be used in the reverse sense, as indicating that the law of conservation of mass is experimentally upheld to a very high degree of accuracy. As examples may be cited Stas' complete synthesis of silver iodide and complete analysis of silver iodate.

For the synthesis of silver iodide, a weighed quantity of iodine was converted into ammonium iodide by dissolving it in ammonium sulphite, all reagents being elaborately purified. A quantity of pure silver, slightly less than that required to react with the iodine, was dissolved in nitric acid and converted into silver sulphate

by evaporation with sulphuric acid. The solutions of silver sulphate and ammonium iodide were mixed, and exact equivalence of iodine and silver obtained by titrating with a standard solution of silver sulphate. The silver iodide formed was filtered off and weighed, allowance being made for the solubility of silver iodide.

In one experiment, the weight of iodine taken

	= 44.7599 gm.
Silver weighed out	= 38.0620 gm.
Silver added as Ag_2SO_4 solution	= 0.0175 gm.
<hr/>	
Weight of Ag + I taken	= 82.8394 gm.
Weight of AgI formed	= 82.8375 gm.
Discrepancy	= -0.0019 gm.

or 2.3 pts. per 100,000.

i.e., the law of conservation of mass holds experimentally to at least this degree of accuracy.

The complete analysis of silver iodate was even more remarkable for its accuracy. A weighed quantity of silver iodate was decomposed by heating, and the oxygen liberated absorbed by red hot copper. The increase in weight of the copper plus the weight of the silver iodide remaining was then compared with the weight of silver iodate taken. During the experiment a slow current of nitrogen was passed through the apparatus, but the bulbs in which the silver iodate and the copper were heated were weighed evacuated before and after the experiment. To compensate for changes in the buoyancy of the air, each was weighed against a counterpoise of the same external volume. It was possible to reproduce the absolute weight of the whole apparatus, amounting to 2,000 gm., to within 0.005 gm. before and after the experiment—a most remarkable achievement.

In one determination,

Weight of AgIO_3 taken	= 156.7859 gm.
Wt. of AgI + increase in wt. of Cu.	= 156.7839 gm.

Wt. of AgIO_3 - (wt. of AgI + wt. of 30) = -0.0020 gm.
or 1.4 pts. per 100,000.

While it is true that the great concordance of the results of Stas must, as later work has shown, have been enhanced to some small degree by mutually compensating errors, from the viewpoint of the present considerations it remains as showing that the law of conservation of mass is experimentally realised to a very high degree of accuracy.

MORLEY'S COMPLETE SYNTHESIS OF WATER

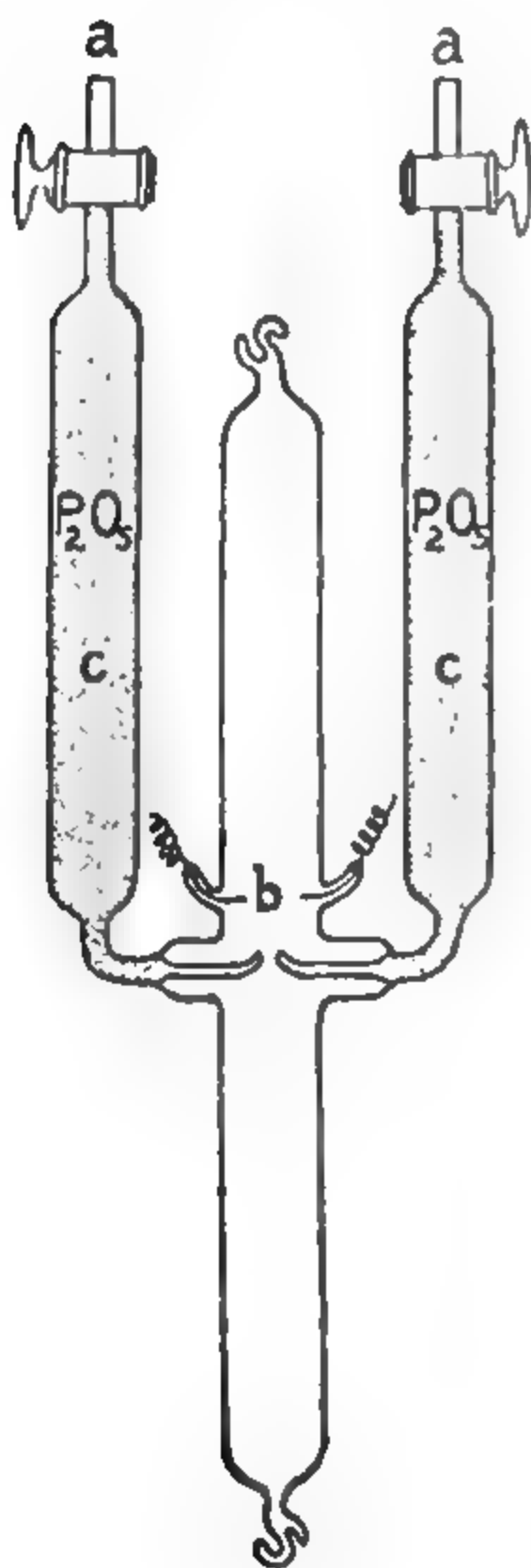


FIG. 1

The investigations of Morley (*Smithsonian Contributions to Knowledge*, 1895) on the combining ratio of oxygen and hydrogen provide further incidental material for the experimental examination of the law of conservation of mass. This work consisted of a complete synthesis of water, and by its remarkable accuracy and the experimental skill involved it stands out as a classical research which well repays the study of the original paper.

Oxygen, prepared by heating potassium chlorate, was stored in large glass globes, the difference in weight of which before and after an experiment gave the weight of oxygen used. Electrolytic hydrogen was absorbed in palladium and freed by heating; the bulb of palladium was similarly weighed before and after each experiment. All weighings were carried out against counterpoises of the same volume as the object weighed. In performing a determination,

oxygen was led into one side tube (a) of the weighed, evacuated reaction tube (*Fig. 1*), the lower end of which was cooled. Hydrogen was led in through the other tube and ignited by a spark across the electrodes (b). Oxygen and hydrogen were then admitted in the appropriate proportions until sufficient water had formed, when the stream of gas was stopped and the small quantity of residual gas inside the tube pumped out and analysed. Loss of water was prevented by the phosphorus pentoxide tubes (c). The weights of hydrogen and of oxygen used were then determined, and the weight of water formed found from the increase in weight of the reaction vessel.

In one particular experiment,

Weight of hydrogen taken	= 3.8225 gm.
Weight of oxygen taken	= 30.3497 gm.
<hr/>	
Weight of hydrogen + weight of oxygen	= 34.1722 gm.
Weight of water found	= 34.1742 gm.
Discrepancy	= + 0.0020 gm.

or 6 pts. per 100,000.

The errors in a whole series of experiments were equally small and equally often positive and negative; i.e., it may be asserted that Morley's experiments indicate that the law of conservation of mass is valid to within a very small experimental error; no evidence is afforded of the real gain or loss of mass of the system during the course of a chemical reaction.

THE WORK OF LANDOLT

The only experiments which have been performed since the days of Lavoisier directly with a view to testing the validity of the law of conservation of mass are those of Landolt (1893-1908) and of Heydweiler (1901). It was the object of these researches to ascertain whether, although the law holds to a high degree of accuracy—as follows from the complete analyses and syntheses of Stas, and of Morley—minute deviations might not nevertheless exist. An exceedingly high degree of accuracy was therefore aimed at. Various reactions in aqueous solu-

tion were carried out in sealed vessels, which were weighed before and after the reaction to a few hundredths of a milligram. The solutions were contained in the two limbs of \cap -shaped glass vessels (*Fig. 2*) and the reaction carried out by tilting the tube so that the solutions mixed. Duplicate tubes of identical volume and of the same surface area were used as counterpoises to compensate for the buoyancy of the air. Simple reactions were chosen in which the heat evolution was fairly small, namely,

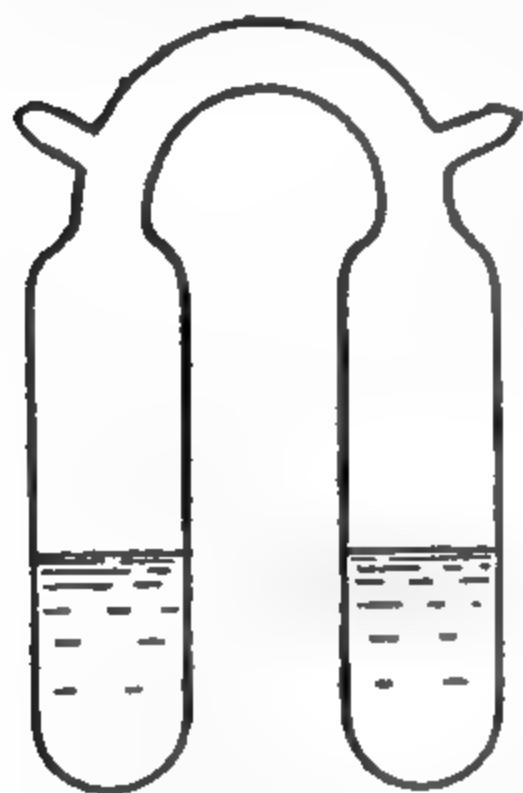


FIG. 2.

- (a) The reduction of silver sulphate by ferrous sulphate.
- (b) The formation of iodine from iodic acid and hydriodic acid.
- (c) The oxidation of sodium sulphite by iodine.
- (d) The displacement of copper from copper sulphate by means of iron.
- (e) The electrolysis of cadmium iodide.
- (f) The decomposition of chloral hydrate by potash.

From 100 to 300 gm. of the reacting substances were taken, the total weight of each apparatus being about 400 to 800 gm.

In Landolt's first series (*Z. Phys. Chem.* 1893, **12**, 1) it was found that, especially with reactions (a) and (b), the differences in weight observed, though small, were larger than the error of weighing, and almost uniformly negative in sign. This result was confirmed by Heydweiler (1901), and Landolt was inclined to view the results as indicating the real destruction of mass, perhaps similar to the newly discovered radioactive changes. Subsequent work by Landolt, however (*Z. Phys. Chem.* 1908, **64**, 581), showed that this effect was illusory. The heating effects of the reaction give rise to expansion of the apparatus, complete recovery from which is slow, which causes the buoyancy effect of the air to differ from that originally counterpoised. Moreover, the film of

water vapour "adsorbed" on the surface of the glass is disturbed by the heating, and requires a long period for the re-attainment of its original value. Landolt repeated a portion of his work, taking great precautions to eliminate completely these sources of error, and determined the approximate correction to be applied to his earlier results. He was then able to show that during the various reactions investigated, quantities of reacting substances of the order of 200 gms. could have changed in weight by certainly not more than 0.024 mgm., the estimated maximum experimental error, and that the observed variations were equally often positive and negative—i.e., distributed quite at random.

The highest possible value for deviation of the law of conservation of mass from exact truth is thereby placed at about one part in ten million, a limit which Manley claims to have pushed further to one part in a hundred million. While, therefore, modern considerations as to the relation between matter and energy may have affected the philosophical basis of the law, as an experimental fact the law is established to the utmost degree of refinement.

THE LAW OF CONSTANT PROPORTIONS

The law of constant proportions states that elements combine in fixed proportions by weight to form compounds.

The law, though to-day firmly grounded as axiomatic, has been in the past the subject of interesting controversy. Between 1800 and 1808, C. L. Berthollet maintained that fixity of composition was not a necessary characteristic of chemical compounds. J. L. Proust, on the other hand, held that the law of constant composition was valid, bringing forward as evidence analyses of many substances, natural and artificial in origin, prepared from many sources, which showed that the composition of any given compound was the same, whatever its source of origin or mode of preparation. He was able to show that the examples cited by Berthollet were, in fact, not

applicable, but that the substances involved—basic salts, solutions, glasses, etc.—were not homogeneous compounds, but actually mixtures.

This conclusion of Proust's, strengthened by the steadily increasing analytical accuracy attained by Berzelius and his pupils, firmly established the law of constant proportions. In 1859, however, C. G. de Marignac suggested that, although the law was plainly an almost exact representation of the facts, the composition of compounds might nevertheless vary between very narrow limits. Partly as a consequence of this suggestion, J. S. Stas undertook a very careful examination of the question. One portion of this work, the determination of the composition of silver chloride prepared in different ways, may be quoted. Silver chloride was prepared by four distinct methods.

- A. Silver was burned in chlorine directly to silver chloride.
- B. Silver was dissolved in nitric acid, hydrochloric acid gas led in, and the whole evaporated in the same vessel.
- C. Silver was dissolved in nitric acid, hydrochloric acid added, and the precipitated silver chloride collected and washed with dilute nitric acid. Silver chloride dissolved in the washings was recovered by evaporation.
- D. Silver was dissolved in nitric acid, and silver chloride precipitated by addition of pure ammonium chloride.

The results, each the mean of several independent experiments, were as shown :

100 pts. by weight of silver yielded,	
by method A	132.8425 pts. silver chloride.
by method B	132.8475 pts.
by method C	132.848 pts.
by method D	132.842 pts.

i.e., within exceedingly narrow limits of experimental error, the composition of silver chloride was the same whatever the method of preparation employed. A

similar result was obtained from the investigation on the composition of ammonium chloride, and it has ever since been concluded that the precise results of Stas, coupled with the accumulated experience of chemists generally, justify the classification of the law of constant proportions as an exact law.

THE LAW OF MULTIPLE PROPORTIONS

The law of multiple proportions governs the relations between the compounds formed when two elements can combine in more than one ratio. The law states that where two elements can combine in two or more ways, the weights of the one element which severally combine with a constant weight of the other element bear to one another a simple ratio.

Thus, nitrogen and oxygen combine to form five compounds, whose percentage compositions are:—

Nitrogen	63.66	46.67	36.85	30.44	25.93%
Oxygen	36.34	53.33	63.15	69.56	74.07%

Considering the weight of oxygen combined with a constant weight of nitrogen, *e.g.*, 63.66 parts, we have in

the second compound $\frac{63.66 \times 53.33}{46.67} = 72.70$ pts. Calculat-

ing the remaining values similarly, we find that 63.66 parts by weight of nitrogen are combined with

36.35 72.70 109.05 145.40 178.75 parts
of oxygen respectively, amounts which are in the ratio

1 : 2 : 3 : 4 : 5

Hence the five oxides of nitrogen are seen to conform to the law of multiple proportions.

It is of historical interest that the law of multiple proportions, the experimental basis of which was established independently by Wollaston and by Berzelius, was first enunciated by John Dalton as a logical consequence of his atomic theory, rather than as, primarily, a generalisation connecting known facts,

THE LAW OF EQUIVALENT OR COMBINING PROPORTIONS

The weights of the various elements which combine with a certain fixed weight of some other element—selected arbitrarily as a standard of reference—(or multiples thereof) combine also with one another.

That is to say, if two elements A and B unite with the element C, then, if A and B combine, they will do so in the proportions of those weights which combine with the same weight of C (or, in some cases, in simple multiples of those proportions).

Thus, as an example,

28 pts. silicon combine with $\left\{ \begin{array}{l} 12 \text{ pts. carbon} \\ \text{or} \\ 32 \text{ pts. oxygen} \end{array} \right.$

and,

12 pts. carbon combine with 32 pts. oxygen.

The proportions by weight in which the elements combine are therefore closely interrelated, and to every element may be assigned a number representing the number of parts by weight of the element in question—measured relative to some arbitrary standard—which will unite with a fixed weight of the substance of reference. This quantity, characteristic for each element, is termed the *combining weight* or *equivalent*. It should be stated that one and the same element may possess more than one equivalent weight, since elements can combine in more than one proportion.

In any chemical change, one equivalent of one element reacts with one equivalent of another element, never one equivalent of the one with more than one of the other. This conception of the equivalence of definite amounts of substances may be extended, as will be seen in Chapter VI to include compound radicals which take part in reactions without splitting up.

CHEMICAL EQUIVALENTS

Hydrogen, as the lightest element, was originally taken as the reference substance, and was assigned the

equivalent 1.000. The equivalent of oxygen on this scale is 7.94. There are, however, few elements which combine directly with hydrogen or displace hydrogen directly from acids or alkalis: it is more convenient to employ as standard oxygen, which permits of the comparison being made far more directly. Oxygen is accordingly taken as standard, with the equivalent 8.000; that of hydrogen becomes 1.008. Further, as a consequence of the experimental methods adopted for the determination of equivalent weights, comparison is often made against chlorine or bromine. It is found that 1.008 parts of hydrogen combine with 35.457 parts by weight of chlorine or with 79.916 parts of bromine. Hence one equivalent of any other element will also combine with these amounts.

We may accordingly define equivalent weights as follows:—

The equivalent weight of an element is that weight of the element which combines with or which replaces 8.000 parts by weight of oxygen, or 1.008 parts of hydrogen, or 35.46 parts chlorine—or, in fact, a quantity of any other substance itself equivalent to these amounts.

The equivalent weight of an element in grams is termed the gram-equivalent; *e.g.*, one gram-equivalent of chlorine weighs 35.46 gm.

THE DETERMINATION OF EQUIVALENTS

The principal methods adopted for the determination of equivalents will now be considered.

(1) Conversion of the element into its oxide, or, alternatively, reduction of the oxide to the element. This method has the advantage of measuring the equivalent directly relative to the standard substance, oxygen.

Example 1. 6.4406 gm. of carbon in the form of diamond yielded on combustion 23.6114 gm. of carbon dioxide.

Calculate the equivalent of carbon.

From the data $(23.6114 - 6.4406) = 17.1708$ gm. of oxygen, combined with 6.4406 gm. of carbon

$$\therefore 8.000 \text{ gm. of oxygen combined with } \frac{8.00 \times 6.4406}{17.1708} \text{ gm. of carbon} \\ = 3.001 \text{ gm.}$$

Equivalent of carbon = 3.001.

Example 2. 2.272 gm. of platinum oxide left, on strong ignition, a residue of the metal weighing 1.952 gm.

What is the equivalent of platinum?

$$\begin{array}{l} 0.320 \text{ gm. oxygen unite with } 1.952 \text{ gm. of platinum.} \\ \therefore 8.000 \text{ ,, ,, ,, ,, } \frac{8.00 \times 1.952}{0.320} \text{ gm. of platinum} \\ = 48.80 \text{ gm.} \end{array}$$

Equivalent of platinum = 48.80.

(2) **Measurement of the hydrogen displaced.**
In the case of elements which dissolve in acids or alkalis with the evolution of hydrogen, it is convenient to measure the volume of hydrogen liberated when a known weight of element is dissolved. Then, the equivalent of the element (in grams) is that weight of the element which liberates a volume of hydrogen equal to that occupied by 1.008 gm. It is unnecessary to calculate the weight of hydrogen liberated, since this volume of one gram-equivalent is known.

1.008 gm. hydrogen occupy, at 0°C and 760 mm. pressure a volume of 11,205 c.c. The equivalent of an element is therefore the weight displacing 11,205 c.c. hydrogen, measured at 0°C and 760 mm. (Normal Temperature and Pressure, written N.T.P. or S.T.P.) Since the volumes of gases are usually measured in the laboratory under differing conditions of temperature and pressure, correction must be made to the standard conditions.

The Combined Gas Law.

The variation of the volume of gases with pressure, at constant temperature, is given by Boyle's law,

$$p_1 V_1 = p_2 V_2$$

The variation of volume with temperature, at constant pressure, is given by Charles' law,

$$V_t = V_0 \left(1 + \frac{t}{273}\right) = V_0 \left(\frac{273+t}{273}\right)$$

or, writing $(273+t) = T_1$, the absolute temperature, and rearranging

$$\frac{V_1}{T_1} = \frac{V_0}{T_0}$$

Take a volume of gas V_1 , at temperature T_1 absolute, under a pressure p_1 . It is required to find its volume V_2 at temperature T_2 and pressure p_2 .

V_1 $p_1 \quad T_1$

V $p_2 \quad T_1$

V_2 $p_2 \quad T_2$

First, at the temperature T_1 , alter the pressure to p_2 . The volume becomes V , where

$$p_1 V_1 = p_2 V \quad \dots \dots \dots (1)$$

Second, keeping the pressure constant at p_2 , alter the temperature to T_2 . The volume now changes from V to V_2 ,

By Charles' law, $\frac{V}{T_1} = \frac{V_2}{T_2} \quad \dots \dots \dots (2)$

Substituting from (1) the value $V = \frac{p_1}{p_2} V_1$

$$\begin{aligned} \frac{p_1 V_1}{p_2 T_1} &= \frac{V_2}{T_2} \\ \text{i.e.,} \quad \frac{p_1 V_1}{T_1} &= \frac{p_2 V_2}{T_2} \\ \text{or} \quad V_2 &= \frac{p_1 T_2}{p_2 T_1} V_1 \end{aligned}$$

Example. What is the volume at 0° and 760 mm. of 237.5 c.c. gas, measured at 22° and 737 mm?

$$T_1 = 273 + 22 = 295^\circ$$

$$T_2 = 273^\circ$$

$$p_1 = 737 \text{ mm.}$$

$$p_2 = 760 \text{ mm.}$$

$$V_2 = \frac{737}{760} \times \frac{273}{295} \times 237.5 \text{ c.c.} = 213.1 \text{ c.c.}$$

DALTON'S LAW OF PARTIAL PRESSURES

The volume of hydrogen or other gas evolved in a reaction is frequently measured over water. The gas then contains water vapour, and the total pressure exerted by the gas in the gas burette or eudiometer is due, not solely to the hydrogen, but in part to the water vapour present.

Dalton found that in such cases, where two or more gases or vapours are present which have no chemical action upon one another, each gas exerts the same pressure as if it alone filled the space, i.e., the total pressure of a mixture of gases is the sum of the partial pressures of the various constituents. In such a case as that under consideration, where a gas is measured over water, the space will be filled with saturated water vapour, and the partial pressure of water vapour is equal to the vapour pressure of water at the temperature of the experiment.

Thus, if the total pressure of the hydrogen, collected and measured over water in an equivalent determination, be p mm.,

$$p = p_H + p_{H_2O}$$

where p_{H_2O} , the vapour pressure of water at the temperature of experiment, may be found by reference to tables.

Example. What is the volume at N.T.P. of 155 c.c. hydrogen collected and measured over water at 10° and 747 mm. pressure?

Pressure of wet gas	= 747 mm.
Vapour pressure of water, 10°C	= 9.2 mm.
\therefore Partial pressure of hydrogen	= 738 mm. approx.

$$\text{volume at N.T.P.} = \frac{738}{760} \times \frac{273}{283} \times 155 \text{ c.c.}$$

$$= 145.0 \text{ c.c.}$$

These relationships may now be applied to the determination of equivalents by measurement of the hydrogen liberated.

Example. 0.1265 gm. sodium was covered with paraffin and water added. The sodium reacted with the water, 68.4 c.c. hydrogen being liberated, measured at 25° and 771 mm. pressure. Find the equivalent of sodium.

Total pressure of hydrogen+water vapour = 771 mm.
 Vapour pressure of water at 25° = 24 mm.
 \therefore Partial pressure of hydrogen = 747 mm.

0.1265 gm. of sodium displaces 68.4 c.c. of hydrogen, measured at 25° and 747 mm.

$$= \frac{747}{760} \times \frac{273}{298} \times 68.4 \text{ c.c. hydrogen at N.T.P.}$$

1 equivalent of sodium liberates, by definition, 11,205 c.c. hydrogen at N.T.P.

\therefore 11,205 c.c. hydrogen are liberated by

$$\frac{11,205}{68.4} \times \frac{760}{747} \times \frac{298}{273} \times 0.1265 \text{ gm. of sodium} \\ = 23.00 \text{ gm.}$$

Equivalent of sodium = 23.00

(3) The conversion of the element to its chloride or bromide, or the reduction of the chloride or bromide to the element.

Example. 24.289 gm. of nickel bromide gave on reduction 6.523 gm. nickel. Calculate the equivalent of nickel.

In nickel bromide,

17.767 gm. of bromine are combined with 6.523 gm. of nickel. The equivalent of nickel is the weight combining with 79.92 parts of bromine.

Hence, 79.92 parts of bromine are combined with

$$\frac{79.92 \times 6.523}{17.767} \text{ pts. of nickel}$$

$$= 29.35 \text{ parts.}$$

Equivalent of nickel = 29.35.

(4) Displacement of the element from one of its compounds by an element of known equivalent.

Example. 0.1275 gm. of cadmium was immersed in silver nitrate solution, and the silver displaced was collected and its weight was found to be 0.2457 gm. Find the equivalent of cadmium, given that the equivalent of silver equals 107.9.

0.2457 gm. of silver is displaced by 0.1275 gm. cadmium.
 107.9 gm. „ are „ $\frac{107.9 \times 0.1275}{0.2457}$ gm. „
 = 56.0 gm.

Equivalent of cadmium = 56.0.

INDIRECT METHODS

The methods of equivalent determination dealt with above provide in each case a means of comparing the equivalent of the element in question with that of one element of known equivalent—oxygen, hydrogen, chlorine, etc. In actual practice, the methods adopted for the most accurate determination of equivalent weights are usually less direct, requiring a knowledge of the atomic weights of two or more of the “reference elements.” A consideration of these methods of equivalent determination is therefore deferred until the chapter on Atomic weights (Chapter IV, *q.v.*) where the matter is discussed at length.

PROBLEMS ON THE LAWS OF COMBINATION.

(Answers to those questions with odd numbers will be found at the end of the book)

THE LAW OF MULTIPLE PROPORTIONS

- 1 The oxides of manganese contain 77.44%, 69.60%, 63.18%, 53.37% and 49.52% of manganese respectively. Show that these figures are in accord with the law of multiple proportions.
- 2 Sulphides of arsenic exist containing 29.99%, 39.05% and 51.70% of sulphur respectively. Show that they conform to the law of multiple proportions.
- 3 Illustrate the law of multiple proportions from the composition of the following silicon compounds. (a) 16.64% Si, 83.36% Cl; (b) 21.02% Si, 78.98% Cl; (c) 23.03% Si, 76.97% Cl.
- 4 Show that the existence of oxides of sulphur containing respectively 57.20%, 50.06%, 40.06% and 36.44% of sulphur does not contravene the law of multiple proportions.
- 5 Cæsium combines with iodine to form compounds which contain 51.13%, 25.86% and 20.73% of the metal respectively. Use these figures to illustrate the law of multiple proportions.

REDUCTION OF GAS VOLUMES

- 6 What would be the volume at 15° and 757 mm., dry, of a volume of hydrogen measuring 227 c.c. over water at 12° and 762 mm. pressure? (Pressure of water vapour at $12^{\circ} = 10.5$ mm.)
- 7 What is the volume at N.T.P. of 4.16 c.c. hydrogen measured over water at 18° and 345 mm. pressure? (Pressure of water vapour at $18^{\circ} = 15.4$ mm.)
- 8 What pressure would be developed on heating to 350° C. a sealed tube originally containing air at 16° and 763 mm. pressure? At what temperature would the pressure attain 3 atmospheres?
- 9 The vapour pressure of alcohol at 15° is 39 mm. What volume would 1 litre of hydrogen (measured at N.T.P.) occupy over alcohol at 15° , when the barometric pressure was 771 mm.?
- 10 147 c.c. of stibine, measured dry at 17° and 761 mm. decomposed on standing over water, and the volume changed to 221 c.c., the wet gas being measured at 15° and 764 mm. pressure. In what ratio has the gas expanded?

PROBLEMS ON CHEMICAL EQUIVALENTS

- 11 Cobalt oxide contains 78.613% of cobalt. Calculate the equivalent of cobalt.
- 12 What is the equivalent of zinc, if zinc oxide contains 80.31% of its weight of zinc.
- 13 Find the equivalent of molybdenum, given that molybdenum oxide contains 66.49% of the metal.
- 14 1.7999 gm. of tungsten oxide yielded on reduction 1.4724 gm. of tungsten. Calculate the chemical equivalent of tungsten.
- 15 What is the equivalent of nickel, if 1.6845 gm of nickel were obtained by reduction of 2.1434 gm. of nickel oxide?
- ✓ 16 0.1073 gm. of magnesium was dissolved in dilute sulphuric acid. 106.9 c.c. hydrogen were evolved, measured over water at 16° and 758 mm. pressure. Find the equivalent of magnesium.
- 17 When 0.3014 gm. of iron wire was treated with hydrochloric acid, 131.9 c.c. hydrogen were liberated. Measurement was carried out on the dry gas, collected over mercury, at 21° and 750 mm. pressure. Calculate the equivalent of iron.
- 18 0.1843 gm. of aluminium foil was dissolved in caustic potash solution. 247.2 c.c. hydrogen, measured at 15° and 754 mm. over water, were evolved. Calculate the equivalent of aluminium.

- 19 If 407.6 c.c. of hydrogen, measured wet at 7° and 764 mm., were evolved when 1.037 gm. of nickel dissolved in hydrochloric acid, what is the equivalent of nickel?
- 20 By the solution of 0.1475 gm. of pure zinc in dilute sulphuric acid, 54.4 c.c. hydrogen were obtained, measured at 12°. The water level inside the eudiometer was 13 cm. above the free surface of the water in the levelling tube. The barometric pressure was 757 mm. Find from these data the equivalent of zinc.
- 21 10.057 gm. of mercuric chloride were decomposed by electrolysis, 7.431 gm. of mercury being obtained. What is the equivalent of mercury?
- 22 0.47319 gm. of cadmium was obtained when 0.77264 gm. of cadmium chloride was decomposed electrolytically. Find the equivalent of cadmium.
- 23 11.087 gm. of tin bromide were obtained by the action of bromine on 3.006 gm. of tin. Calculate the equivalent of tin.
- 24 The weight of tellurium bromide made from 0.3738 gm. of tellurium was 1.3108 gm. Determine the equivalent of tellurium.
- 25 What is the chemical equivalent of tungsten, if 10.433 gm. of tungsten chloride yielded on reduction 4.837 gm. of tungsten?
- 26 9.0684 gm. of silver were dissolved in nitric acid, and an excess of pure ammonium chloride added. The precipitate of silver chloride obtained weighed 12.044 gm. Find the equivalent of silver.
- 27 Stas found that 97.145 gm. of silver bromide were obtained from 55.804 gm. of silver. What value do these figures give for the equivalent of silver?
- 28 3.047 gm. of gold bromide were reduced in a current of hydrogen. The gold remaining weighed 1.375 gm. Find the equivalent of gold.
- 29 2.075 gm. of tungsten were burned in chlorine, 4.475 gm. of tungsten chloride being formed. Calculate the equivalent of tungsten.
- 30 Calculate the equivalent of osmium, if 3.140 gm. of the metal were left after reduction of 5.473 gm. of osmium chloride.
- 31 0.5829 gm. of cobalt, immersed in a solution of gold bromide, displaced 1.2913 gm. of gold from solution. If the chemical equivalent of gold is 65.74, calculate that of cobalt.
- 32 0.6006 gm. of silver was displaced from a solution of silver nitrate by the action of 0.5765 gm. of lead. The equivalent of silver is 107.9. Calculate the equivalent of lead.
- 33 1.375 gm. of zinc displaced 4.540 gm. of silver from solution. Find the equivalent of zinc, given that the equivalent of silver = 107.9.

- 34 When 4.4406 gm. of silver were heated in selenium vapour, 6.0657 gm. silver selenide were formed. Find the equivalent of selenium. (Equivalent of silver = 107.88.)
- 35 By the combination of 4.723 gm. of silver with iodine, 10.271 gm. of silver iodide were obtained. This, on heating in a stream of chlorine, left a residue of silver chloride weighing 6.270 gm. The equivalent of chlorine is 35.46. Calculate the equivalent of iodine.

CHAPTER II

THE ATOMIC THEORY

THE ATOMIC STRUCTURE OF MATTER

In view of the simplicity of the laws of combination which have been considered in the previous chapter, it would seem that there must be some underlying explanation in the ultimate structure of matter.

There are two obvious hypotheses which have been applied to the structure of matter—(a) that matter is *continuous* and completely fills the space which it occupies, and (b) that it is *discontinuous*, consisting of small particles separated or partially separated by space. Both these hypotheses were familiar in more or less definite form to the Greek philosophers, but it was not until the beginning of the present scientific age that they were given any quantitative significance, when Newton gave a mathematical proof of Boyle's law on the assumption that gases were composed of discontinuous particles of matter which repelled one another. The formulation of the atomic theory in a way which could co-ordinate all known facts and give an explanation of the quantitative laws of chemistry, and which led to the extension of the scope and accuracy of the scientific method is undoubtedly due to John Dalton, a Manchester schoolmaster (1803).

Dalton put forward the following postulates :—

(1) Elements are composed of minute indivisible particles of matter, or atoms, which are unchanged during any chemical change.

(2) All atoms of the same element are the same in all respects, notably in weight, but are different from the atoms of all other elements.

(3) Chemical combination takes place by the union of atoms in simple numerical ratios; *e.g.*, one atom of an element A will combine with one atom (or two or three atoms) of an element B to form a compound.

The absolute weights of the atoms are exceedingly small and could not be estimated by Dalton. (The absolute mass of the hydrogen atom is now known to be about 1.66×10^{-24} gm.) He therefore confined his attention to their relative weights, taking the weight of the lightest atom, hydrogen, as unity. The atomic weight was thus the ratio of the weight of an atom of the element under consideration to the weight of an atom of hydrogen. As has been pointed out in the previous chapter in connection with equivalent weights, oxygen is now taken as the standard. On this scale the atomic weight of oxygen is 16.000 and that of hydrogen becomes 1.008.

THE LAWS OF COMBINATION AND THE ATOMIC THEORY

The laws discussed in the last chapter are experimentally true and do not depend on any theory, but it will be seen that they follow as a direct consequence of the atomic theory which thus gives a rational explanation of these experimental results.

(1) Since atoms are indestructible, and preserve their identity and hence their masses, during any chemical change, the total mass of the atoms will be the same before and after the reaction. (*Law of conservation of mass.*)

(2) As a compound is composed of two, three or more atoms which are always of the same kinds and in the same numbers in any given compound, then each compound will always contain the same elements in the same proportions. (*Law of constant proportions.*)

(3) If two elements unite to form more than one compound, then the numbers of atoms of the one element combined with one atom of the other element in one compound will bear a simple ratio to the number com-

bined with one atom in the other compound, and hence the weight of this element combined with a fixed weight of the other element in the first compound will bear a simple ratio to the weight combined with the same fixed weight in the other compound. (*Law of multiple proportions.*)

(4) As atoms of a single element always have the same weight, and as elements always combine in simple proportions by atoms, then the weights of atoms combining will be in the ratios of their atomic weights or simple fractions of this. Hence follows the *law of equivalent proportions*. The atomic weight, as will be seen later (see p. 73), is always a simple multiple of the equivalent weight of the same element.

DIFFICULTIES OF THE ATOMIC THEORY

Dalton's original theory provided no means of determining the relative atomic weights of the elements, because it was impossible to estimate the numbers of atoms of each element that went to compose the complex atom or molecule which they formed. Thus in the compound water, which is formed by the union of oxygen and hydrogen, it is known that the relative weights are 8:1. If, then, the molecule of water is composed of only one atom of oxygen and one atom of hydrogen, that means that the atom of oxygen is eight times as heavy as the atom of hydrogen (or the atomic weight of oxygen is 8). If, however, the molecule of water is composed of two atoms of hydrogen and one of oxygen, the oxygen atom will be eight times as heavy as two atoms of hydrogen or sixteen times as heavy as one atom of hydrogen (the atomic weight of oxygen is 16). Again, if there are three atoms of hydrogen and one of oxygen in the water molecule, the atom of oxygen will be eight times as heavy as three, or twenty-four times as heavy as one atom of hydrogen (atomic weight of oxygen is 24).

Thus, it is seen that the atomic weight is a simple multiple of the equivalent weight of an element, but the classical atomic theory gives no indication of what

multiple. Dalton was compelled to fall back upon empirical rules to overcome this difficulty. He assumed that if only one compound of two elements is known, it will be as simple as possible. Thus water and ammonia were erroneously assumed to be binary compounds—i.e., to be composed of one atom of each of the two elements from which they are formed. In spite of brilliant chemical work by Berzelius, who extended the chemical evidence for the structure of compounds, no satisfactory method of determining atomic weights was forthcoming for half a century, so many chemists who were not satisfied with the arbitrary weights based on Dalton's rules fell back on the use of equivalent weights as being more certain.

A still more serious difficulty in the way of Dalton's theory was due to an erroneous assumption that the particles of elements were simple atoms. The true theory, that explained the contradiction which arose from this and led the way to a true knowledge of atomic weights and the composition of compounds, was given by Avogadro about this time, but did not secure recognition. His theory will be discussed in the next chapter.

THE MODERN THEORY OF THE STRUCTURE OF MATTER

Developments in chemistry and physics during the present century have led to a much more extensive knowledge of the composition and behaviour of matter, as well as of the conditions governing its various kinds of existence, than was ever foreshadowed by the classical atomic theory of Dalton.

Researches on the discharge of electricity through gases at low pressures and on the behaviour of radioactive substances such as the compounds of radium and uranium led to a certain conclusion that the atom was not the solid indivisible particle that it had been assumed to be, but that just as any material object is discontinuous in composition, being composed of atoms and space, so the atom itself is discontinuous in character, by far the greater part being empty space.

While the atom as a whole is electrically neutral, it is to be regarded as an aggregate of electric charges. The atom of any element consists of a very small positively charged nucleus in which the mass of the atom is concentrated, surrounded by one or more negatively charged electrons which are assumed to revolve in orbits at various levels around the nucleus. The atomic nucleus is also complex in structure and contains one or more protons which are unit positive charges of electricity and, except in the case of hydrogen, one or more electrons. The proton is of unit mass; thus the hydrogen atom contains one proton and has the atomic weight one, helium has four protons and atomic weight four.

The mass of the electron is negligible compared with that of the proton, but it is nevertheless the extra-nuclear electrons that determine the chemical properties of the atom and give the individual characteristics of each element. It will be seen that all matter is built up of the same fundamental constituents and that the differences in behaviour of the different elements are due to the different numbers and the different arrangements of electrons and protons. As the electron is a unit negative charge of electricity and the proton is a unit positive charge, and the atom is electrically neutral, it follows that each element contains in its atom equal numbers of protons and electrons.

The modern theory of the structure of matter has found striking verification in all branches of chemistry and physics and throws light on many fundamental problems such as the origin of spectra, the method of linkage of the atoms, and the significance of the external symmetry of crystals; nevertheless the classical theory of the atom is in no way invalidated. The laws of combination are experimentally true, and Dalton, in formulating his atomic hypothesis in order to explain them, created a mental picture which is extended rather than destroyed by the modern theories. Calculations based on Dalton's theory are in no way altered by recent developments.

FORMULÆ

The adoption of the atomic theory led to the introduction of a rational chemical nomenclature. Each element was given a symbol, usually the first letter, or the first and another letter of its Latin name. Thus iron (ferrum) is Fe, chlorine is Cl and tin (stannum) is Sn. A full list of the symbols of the elements will be found in the atomic weight table at the end of the book.

It should be remembered that, for example, S does not merely mean sulphur, but a certain weight of sulphur—an atomic weight of sulphur. Again Cl denotes one atom of chlorine or 35.46 parts by weight of chlorine; 35.46 being the weight of the chlorine atom relative to the weight of the oxygen atom 16, or the hydrogen atom 1.008. This weight may be expressed in grams, in pounds, in tons, or in any other measure, as it is a relative weight.

The molecule of the simplest compounds containing one atom each of two different elements is represented by writing the symbols of the constituent elements side by side. Thus, hydrogen chloride which is composed of one atom of hydrogen and one of chlorine, is written HCl. This is known as the formula of the substance. The molecule of sulphur dioxide consists of two atoms of oxygen and one of sulphur and has the formula SO_2 , the small numeral indicating that there are two atoms of oxygen present in the molecule. In just the same way the formula of ammonia is written NH_3 , as there are three atoms of hydrogen and one of nitrogen in this molecule. More complex molecules have naturally more complex formulæ. Thus, sulphuric acid is H_2SO_4 , the molecule consisting of two atoms of hydrogen, one of sulphur and four of oxygen. Aluminium sulphate is written $\text{Al}_2(\text{SO}_4)_3$, the small figure after the bracket multiplying all within; thus, there are three atoms of sulphur, and twelve of oxygen in this molecule.

Just as with the symbols of elements, the formulæ of compounds have a quantitative significance. Thus, HCl represents one molecular weight of hydrogen chloride

Acc. no. = 840

LIBRARY

(36.47) composed of one atomic weight (1.01) of hydrogen and one atomic weight (35.46) of chlorine. If the gram is the unit employed, and this is usual, 36.47 is the molecular weight of the compound expressed in grams, or simply the gram molecular weight.

From what has just been said it will be seen that it is possible to calculate from the formula of a compound and the atomic weights of its constituent elements, its percentage composition. Thus water, with the formula H_2O , has a molecular weight of 18.016 ($2 \times$ atomic weight of hydrogen (i.e., 2×1.008) + 1 atomic weight of oxygen (16)).

This means that 18.016 parts by weight of water will contain 2.016 parts by weight of hydrogen,

100 parts of water will contain $\frac{2.016}{18.016} \times 100 = 11.19\%$ of hydrogen.

Similarly the percentage of oxygen

$$= \frac{16}{18.016} \times 100 = 88.81\%.$$

Analysis will show water to contain 11.19% of hydrogen and 88.81% of oxygen.

A similar method of procedure is used in calculating the percentage composition of more complicated compounds.

Example. Sodium stannate has the formula $Na_2SnO_6 \cdot 3H_2O$. It is required to find its percentage composition.

As the water of crystallisation which is present comes off easily as water and is therefore to be regarded as being combined in the solid as water rather than as hydrogen and oxygen separately, it is usual to express it in terms of the percentage of H_2O rather than as % H and % O.

The molecular weight of sodium stannate will be

$$\begin{aligned} & (2 \times 23) + 118.7 + (3 \times 16) + (3 \times 18) \\ &= 46 + 118.7 + 48 + 54 \\ &= 266.7 \end{aligned}$$

There are two atoms of sodium in the molecule of sodium stannate. The proportion by weight of sodium in the molecule

will therefore be twice the atomic weight of sodium divided by the molecular weight of sodium stannate; the percentage of sodium will be this fraction multiplied by 100.

$$\% \text{ Na} = \frac{46}{266.7} \times 100 = 17.25$$

in the same way :—

$$\% \text{ Sn} = \frac{118.7}{266.7} \times 100 = 44.50$$

$$\% \text{ O} = \frac{48}{266.7} \times 100 = 18.00$$

$$\% \text{ H}_2\text{O} = \frac{54}{266.7} \times 100 = 20.25$$

100.00%

PROBLEMS

(Answers to those questions with odd numbers will be found at the end of the book)

Calculate from the formulæ of the following compounds their percentage composition :—

- | | |
|---------------------------------------|---|
| 36 POCl_3 | 46 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 37 K_2SnCl_6 | 47 $\text{K}_3\text{C}_2\text{I}(\text{CNS})_6$ |
| 38 Na_2SiF_6 | 48 $\text{K}_2\text{SO}_4 \cdot \text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ |
| 39 BaS_2O_6 | 49 $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ |
| 40 Na_3SbS_4 | 50 $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ |
| 41 $\text{C}_{10}\text{H}_7\text{OH}$ | 51 $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ |
| 42 K_2PtBr_6 | 52 $[\text{Pt}(\text{NH}_3)_4](\text{PtCl}_4)$ |
| 43 NaNH_2 | 53 $\text{K}_3\text{Mn}(\text{NO})(\text{CN})_5$ |
| 44 $\text{Mg}_2\text{As}_2\text{O}_7$ | 54 $[\text{Cr}(\text{NH}_3)_4\text{C}_2\text{O}_4]\text{NO}_3 \cdot \text{H}_2\text{O}$ |
| 45 $(\text{NH}_4)_3\text{AlF}_6$ | 55 $\text{PtCl}_2 \cdot 2\text{CO}$ |

CALCULATIONS OF EMPIRICAL FORMULÆ FROM PERCENTAGE COMPOSITION

By means of a process the converse of that used in the last section, it is possible to calculate the simplest formula of a substance from its percentage composition as obtained by analysis.

We shall firstly take the case of water whose percentage composition we have already calculated from its

well established formula, and shall re-calculate its formula from our results by means of the converse process. As we have seen, water contains 11.19% H and 88.81% O. This ratio will represent the ratio of the combining weights of oxygen and hydrogen, so in order to find the atomic proportion, each percentage must be divided by the atomic weight of the element concerned. Thus:—

Element	% Composition	Atomic Proportion	
H	11.19	$\frac{11.19}{1.008}$	= 11.10
O	88.81	$\frac{88.81}{16}$	= 5.55

The ratio of the atoms combining is therefore 11.10 of hydrogen to 5.55 of oxygen, or two of hydrogen to one of oxygen.

∴ the simplest formula of water is H_2O .

Example. Calculate the empirical formula of a substance which gives the following percentage composition:—
Na = 12.04%, B = 11.52%, O = 29.32% and H_2O = 47.12%.

As in the previous example the percentage of each element must be divided by its atomic weight in order to determine the proportion by atoms in which the elements are combined in the compound. This ratio, reduced to the simplest whole numbers, will give the simplest (or *empirical*) formula of the compound.

Element	% Composition	Atomic Proportion	
Na	12.04	$\frac{12.04}{23}$	= 0.52
B	11.52	$\frac{11.52}{11}$	= 1.05
O	29.32	$\frac{29.32}{16}$	= 1.88
H_2O	47.12	$\frac{47.12}{18}$	= 2.68

The atoms and group of atom thus combine in the ratio
Na : B : O : H_2O = 0.52 : 1.05 : 1.88 : 2.68.

Dividing each of these by the lowest number, namely, 0.52, we get Na : B : O : H_2O = 1 : 2 : 3.5 : 5 or = 2 : 4 : 7 : 10.

The simplest formula of the compound is thus
 $Na_2B_4O_7 \cdot 10H_2O$.

It should be noticed that the formulæ calculated from percentage composition are the empirical or simplest formulæ and not the molecular formulæ. Thus, xylene, which has a percentage composition $C = 90.54\%$, $H = 9.46\%$ will be given an empirical formula C_8H_8 , whereas its true or molecular formula is double this, $C_{16}H_{16}$. The molecular formula is thus a simple multiple of the empirical formula. It may be found from the empirical formula if the molecular weight of the compound is known.

In the case of minerals of definite chemical composition it is usual to express the percentage composition in terms of the oxides of the metals and acids which they contain. Thus, dolomite, a double carbonate of calcium and magnesium would be written $CaO = 29.59\%$, $MgO = 22.19\%$, $CO_2 = 48.22\%$. The calculation involved in the determination of its empirical formula is exactly the same as that for simple compounds, except that to find the atomic proportion, the percentage compositions are divided, not by the atomic weights of the elements, but by the molecular weights of the groups of elements. Thus:—

	% Composition	Molecular Proportion	
CaO	29.59	$\frac{29.59}{56}$	= 0.53
MgO	22.19	$\frac{22.19}{40}$	= 0.55
CO ₂	48.22	$\frac{48.22}{44}$	= 1.1

The simplest proportions are $CaO : MgO : CO_2 = 1 : 1 : 2$.

Or the formula is $CaCO_3 \cdot MgCO_3$.

There exist also many groups of minerals whose individual members are composed of equal numbers of atoms similarly combined and which possess the same crystalline form but with varying amounts of the constituent atoms. Thus, there are minerals of the general formula MCO_3 , where M may be a mixture of variable proportions of calcium, magnesium, etc. Such minerals

are termed isomorphous mixtures and are written, *e.g.*, as (Ca,Mg,) CO₃. It is found that if their compositions are converted into the equivalent percentages of one of the elements, the general formula MCO₃ will apply.

Example.

A mineral has the composition : CaO 28.4%, MgO 12.3%, FeO 12.3%, MnO 1.9%, CO₂ 44.4%. Express its composition by a formula.

First, the amounts of CaO equivalent to the other oxides present must be determined.

$$12.3 \text{ pts. of MgO} \equiv \frac{12.3 \times 56}{40.3} = 17.22 \text{ pts. of CaO}$$

$$12.3 \text{ pts. of FeO} \equiv \frac{12.3 \times 56}{72} = 9.57 \text{ pts. of CaO}$$

$$1.9 \text{ pts. of MnO} \equiv \frac{1.9 \times 56}{70} = 1.52 \text{ pts. of CaO}$$

Thus there are $28.4 + 17.22 + 9.57 + 1.52 = 56.7$ parts of typical oxide (in this case CaO) combined with 44.4 parts of CO₂. Hence, by the ordinary method :—

	Atomic Proportion
M ⁿ O	$\frac{56.7}{56} = 1.01$
CO ₂	$\frac{44.4}{44} = 1.01$

The typical composition is therefore MⁿO.CO₂ or MⁿCO₃, where Mⁿ represents Ca,Mg,Fe and Mn. The formula can also be written (Ca,Mg,Fe,Mn)CO₃.

PROBLEMS

(Answers to those questions with odd numbers will be found at the end of the book)

Calculate the empirical formulae of the following compounds from their percentage composition :—

56 Na 32.09%, Zn 45.58%, O 22.32%.

57 S 21.95%, F 78.05%.

58 P 10.80%, O 5.58%, Br 83.62%.

59 Sr 43.01%, Cr 25.57%, O 31.42%.

60 Ag 47.58%, Mn 24.21%, O 28.21%.

61 Fe 30.43%, Cu 34.63%, S 34.94%.

- 62 K 7.03%, Au 35.47%, Br 57.50%.
- 63 H 1.38%, Se 54.54%, O 44.08%.
- 64 H 4.19%, N 29.15%, S 33.36%, O 33.30%.
- ~~65 K 28.22%, Cl 25.59%, O 46.18%.~~
- 66 K 41.95%, C 6.44%, S 51.61%.
- 67 Ca 29.45%, H 0.74%, P 22.78%, O 47.03%.
- 68 Fe 28.50%, CO 71.50%.
- 69 Na 12.84%, H 0.28%, P 8.66%, O 17.87%, H₂O 60.34%.
- 70 Ba 41.23%, Br 47.96%, H₂O 10.81%.
- 71 Cr 20.00%, Cl 40.83%, NH₃ 39.17%.
- 72 Cr 19.54%, Cl 39.90%, H₂O 40.56%.
- 73 Co 27.25%, Cl 49.15%, NH₃ 23.60%.
- 74 C 21.13%, H 2.11%, N 4.93%, Pt 34.37%, Cl 37.46%.
- 75 Hg 62.9%, C 15.1%, H 1.9%, O 20.1%.
- 76 C 55.27%, H 5.27%, N 18.43%, O 21.03%.
- 77 Ba 30.42%, C 31.89%, H 2.21%, O 21.28%, S 14.20%.
- 78 Pb 77.55%, ~~C 17.96%~~, H 4.49%.
- ~~79 Na 19.84%, C 62.05%, H 4.31%, O 13.79%.~~
- 80 Serpentine has the composition:—MgO 43.59%, SiO₂ 43.44%, H₂O 12.97%. By what formula is its composition expressed?
- 81 What is the formula for kaolin, the composition of which is 39.5% MgO, 46.6% SiO₂, 13.9% H₂O.
82. The composition of a felspar is 16.88% K₂O, 18.31% Al₂O₃, 64.82% SiO₂. By what formula can its composition be expressed?
- 83 Carnotite approximates to the composition 9.5% K₂O, 57.6% UO₃, 18.3% V₂O₅, 14.6% H₂O. What is its formula?
- 84 Analysis of a spinel mineral gave the following figures:—MgO 22.4%, CaO 1.7%, MnO 2.2% Al₂O₃ 44.1%, Fe₂O₃ 29.6%. To what type of formula does the mineral approximate?
- 85 A silicate mineral has the composition Na₂O 2.9%, K₂O 17.4%, Al₂O₃ 22.4%, Fe₂O₃ 1.8%, SiO₂ 55.5%. Derive a formula to express its composition.

CHEMICAL EQUATIONS

Chemical reactions may be represented by equations that indicate the re-arrangements of the atoms during the reactions. The symbols or formulæ of the reacting sub-

stances are placed on the left hand side of the equation and are connected by means of an "equals" sign (=) with the symbols or formulæ of the resulting product on the right hand side. Thus, the reaction between iron and sulphuric acid to form ferrous sulphate and hydrogen may be written :—



Although an "equals" sign is used, it does not necessarily mean that the reaction can be reversed as, for example, in this case to form iron and sulphuric acid from ferrous sulphate and hydrogen. Many reactions are, however, reversible, this being indicated by arrows connecting the two sides of the equation. Thus :—



denotes that both calcium oxide reacts with carbon dioxide to produce calcium carbonate, and that calcium carbonate may be split up into calcium oxide and carbon dioxide.

As equations are formed from symbols and formulæ, they denote definite quantities of materials reacting, thus :—



denotes that one molecule of silver nitrate reacts with one molecule of sodium chloride to give one molecule of sodium nitrate plus one of silver chloride; or, applying atomic weights :—

$$\begin{array}{ccccccc} \text{AgNO}_3 & + & \text{NaCl} & = & \text{NaNO}_3 & + & \text{AgCl} \\ 107.9 + 14 + (3 \times 16) + 23 + 35.5 & = & 23 + 14 + (3 \times 16) + 107.9 + 35.5 \\ 169.9 & + & 58.5 & = & 85 & + & 143.4 \end{array}$$

This means that 169.9 parts by weight of silver nitrate would react with 58.5 parts of sodium chloride to form 85 parts of sodium nitrate and 143.4 parts of silver chloride. As in the case of the simple symbols or formulæ these quantities may be expressed as grams, pounds or any other units as long as all of them are in the same system. Applying this in the case above once more; 169.9 grams (or tons) of silver nitrate react with 58.5 grams (or tons) of sodium chloride to form

85 grams (or tons) of sodium nitrate plus 143.4 grams (or tons) of silver chloride.

It will be seen that chemical equations enable calculations to be made on the quantities of materials used or produced in the course of chemical reactions.

Example 1. What weight of lime (CaO) could be obtained by heating 50 kilograms of calcium carbonate?



From the equation it follows that:—

100 parts of cal. carbonate produce	56 parts of cal. oxide.
or 100 Kgm. " " " "	56 Kgm. " " "
i.e., 50 Kgm. " " " "	$\frac{56}{2}$ Kgm. " " "
	= 28 Kgm.

Example 2. What weight of oxygen could be obtained from 100 gm. of potassium chlorate of 83% purity?

100 gm. of impure potassium chlorate contain 83 gm. of pure potassium chlorate.

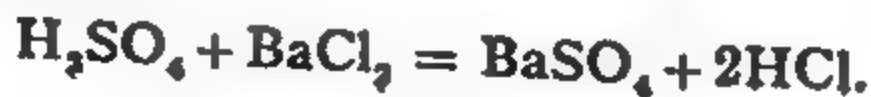


This means that 245 parts by weight of potassium chlorate yield 96 parts of oxygen.

$$\begin{aligned} \therefore 83 \text{ gm. of potassium chlorate yield } \frac{96 \times 83}{245} \text{ gm. O}_2 \\ = 32.53 \text{ gm.} \end{aligned}$$

GRAVIMETRIC ANALYSIS

A quantitative use of chemical formulæ and equations enables the analysis of materials to be carried out by gravimetric means. The substance to be analysed is converted into another compound of known composition which is accurately weighed. From this weight the amount of the required constituent can be found. For example, the weight of sulphate (SO_4) in sulphuric acid might be determined by adding an excess of barium chloride solution.



Barium sulphate which is insoluble and is therefore precipitated thus removes the sulphate quantitatively, and a knowledge of the atomic weights of the elements concerned will enable the amount of SO_4 in BaSO_4 to be calculated.

Example. 2.340 gm. of pure sulphuric acid were diluted with water and the sulphate precipitated with barium chloride solution. The precipitate weighed 5.573 gm. Calculate the percentage of SO_4 in the sulphuric acid.



Weight of barium sulphate formed = 5.573 gm.

The weight of sulphate contained in this will be 5.573 multiplied by the weight of SO_4 and divided by the molecular weight of BaSO_4 .

$$\text{i.e., } \frac{5.573 \times 96}{233.4}$$

$$\therefore \text{Proportion of } \text{SO}_4 \text{ in the acid } = \frac{5.573 \times 96}{233.4 \times 2.340}$$

$$\therefore \text{Proportion of } \text{SO}_4 \text{ in the sulphuric acid} = \frac{5.573 \times 96}{233.4 \times 2.340} \times 100 = 97.97\%$$

By similar means copper can be precipitated as its hydroxide and ignited to the oxide CuO and weighed: iron can be precipitated as ferric hydroxide, ignited and weighed as Fe_2O_3 ; calcium can be precipitated as the insoluble oxalate, ignited to the oxide and weighed: the chlorine in chlorides can be precipitated as insoluble silver chloride, and other methods of a similar character are available for the estimation of most other metals and acid radicals. The procedure is usually more or less complicated owing to the difficulty of obtaining pure precipitates as well as of ensuring complete precipitation. The calculations, however, are uniformly simple and all resemble that in the example above. A further example of one of the estimations with a more complicated procedure will now be worked out.

Example. A sample of basic slag was analysed for phosphorus as follows. 0.556 gm. of the slag was heated with sulphuric acid to convert all the phosphate into phosphoric acid. The phosphate was then purified by precipitating with ammonium molybdate and dissolving the precipitate in ammonia. Magnesia mixture was then added to the solution and the crystalline precipitate of magnesium ammonium phosphate filtered, ignited to magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$) and weighed. The weight was 0.124 gm. Calculate the percentage of phosphorus in the slag.

The phosphorus is all precipitated as $\text{Mg}_2\text{P}_2\text{O}_7$; it is only necessary therefore to calculate the weight of phosphorus contained in 0.124 gm. of this phosphate.

The molecular weight of $\text{Mg}_2\text{P}_2\text{O}_7$ is $(2 \times 24.3) + (2 \times 31) + (7 \times 16)$
 $= 222.6$

\therefore 0.124 gm. of $\text{Mg}_2\text{P}_2\text{O}_7$ contain $\frac{0.124 \times 2 \times 31}{222.6}$ gm. of phosphorus.
 $= 0.0345$ gm.

\therefore phosphorus in the slag $= \frac{0.0345}{0.556} \times 100\%$
 $= 6.21\%$

PROBLEMS ON GRAVIMETRIC RELATIONSHIPS

(Answers to those questions with odd numbers will be found at the end of the book)

- 86 0.1751 gm. of crude sodium sulphate was dissolved in water and treated with barium chloride in excess. The precipitate of barium sulphate obtained weighed 0.2700 gm. What is the percentage purity of the crude sodium sulphate?
- 87 Bone consists of 58% of calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$. Assuming that a 90% yield of elementary phosphorus is obtainable by a manufacturing process, what weight of phosphorus could be manufactured from 150 Kg. of bone?
- 88 0.3145 gm. of hydrated barium bromide, on treatment with silver nitrate, yielded 0.3585 gm. of silver bromide. Find the percentage of water of crystallisation in the barium bromide.
- 89 What is the percentage of chlorine in cadmium chloride, if 0.4364 gm. of silver chloride was obtained from 0.2791 gm. of cadmium chloride on treatment with silver nitrate?
- 90 0.7042 gm. of potassium manganese alum was dissolved in water, acidified with dilute hydrochloric acid, and barium chloride added in excess. 0.6559 gm. of barium sulphate was precipitated. Calculate the percentage of $-\text{SO}_4$ in the alum.

- 91 0.7000 gm. of naturally occurring calcite was dissolved in dilute hydrochloric acid. Ammonium oxalate and ammonia were added, and the precipitated calcium oxalate collected and ignited. 0.3915 gm. of calcium oxide was so obtained. Calculate the percentage of CaCO_3 in the calcite.
- 92 3.075 gm. of an alloy containing phosphorus were dissolved in nitric acid. The phosphorus was determined by precipitating as magnesium ammonium phosphate, ignition of which gave 0.1324 gm. of magnesium pyrophosphate. Find the percentage of phosphorus in the alloy.
- 93 A sample of sterling silver weighing 0.3750 gm. was dissolved in nitric acid and the silver precipitated by addition of ammonium chloride. 0.4739 gm. of silver chloride was precipitated. What proportion of silver does sterling silver contain?
- 94 By the combustion of 0.2040 gm. of succinic acid (containing carbon, hydrogen and oxygen only) 0.3042 gm. of carbon dioxide and 0.0933 gm. of water were formed. Find the percentage composition of succinic acid.
- 95 0.6460 gm. of a mixture of potassium bromide and potassium sulphate was dissolved in water, acidified with nitric acid and silver nitrate added. The precipitate weighed 0.4077 gm. What is the percentage of potassium sulphate in the mixture?
- 96 0.3500 gm. of a compound of sulphur, oxygen and chlorine only was allowed to react with caustic soda. The solution was acidified with nitric acid, and barium nitrate added. After filtration from barium sulphate, the solution was treated with silver nitrate. 0.6054 gm. BaSO_4 and 0.7448 gm. of AgCl were obtained. Find the percentage composition and formula of the compound.
- 97 0.6505 gm. of stainless steel was so treated as to oxidise the chromium it contained to sodium chromate. By addition of mercurous nitrate, mercurous chromate was precipitated, and ignited to chromic oxide, which weighed 0.1140 gm. What is the proportion of chromium in the steel?
- 98 The mother liquors of a Chile saltpetre plant contain 17% of sodium iodate. What weight of iodine could be obtained by treatment of 100 tons of mother liquors?
- 99 0.1570 gm. of native stibnite was fused with sodium peroxide. The melt was extracted with water, and after acidifying, barium chloride precipitated 0.3072 gm. of barium sulphate. What percentage of Sb_2S_3 does the stibnite contain?
- 100 What weight of ferrous sulphide must be taken in order to generate sufficient hydrogen sulphide to precipitate completely the metals from a mixture of 450 gm. of lead nitrate and 320 gm. of cadmium nitrate?

- 101 What weight of sulphuric acid could be manufactured, starting with 10 Kg. of iron pyrites?
- 102 1 gm. of sodium sulphide was dissolved in water, and oxidised by addition of bromine. What weight of barium sulphate would be precipitated on addition of excess of barium chloride?
- 103 During the analysis of realgar, 0.3342 gm. of magnesium pyroarsenate was obtained from a sample of ore weighing 0.2710 gm. What percentage of As_2S_3 does the ore contain?
- 104 A sample of potassium chlorate is contaminated with potassium chloride. 1.244 gm. of the substance left, after strong ignition, a residue weighing 0.8425 gm. Find the percentage purity of the potassium chlorate.
- 105 1.5600 gm. of felspar were treated so as to remove all except sodium and potassium salts. The sodium and potassium chlorides from the spar weighed 0.4735 gm. The chlorides were then converted to sulphates. These weighed 0.5610 gm. What was the percentage of sodium and potassium in the spar?

CHAPTER III

THE MOLECULE AND MOLECULAR WEIGHT

THE LAW OF GAS VOLUMES

In 1781 Cavendish had found that the volumes of hydrogen and oxygen which combine to form water are approximately 2:1. Gay-Lussac and Humboldt confirmed this in 1805, and the former, being impressed by the simplicity of the ratio of volumes of the combining gases, extended his work to a study of gaseous reactions in general. He found, for example, that:—

2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of steam.

1 volume of hydrogen combines with 1 volume of chlorine to form hydrochloric acid.

2 volumes of carbon monoxide combine with 1 volume of oxygen to form 2 volumes of carbon dioxide.

2 volumes of nitric oxide combine with 1 volume of oxygen to form 2 volumes of nitrogen peroxide.

When gases unite there is a simple relation between the volumes of the interacting gases and the volumes of the gaseous products (if any), all volumes being measured under similar conditions of temperature and pressure.

This has been found to be a perfectly general but not an exact law. For example, Morley (see page 4) found that 200.269 volumes of hydrogen combined with 100 volumes of oxygen to form steam, whereas Burt and Edgar (*Phil. Trans.* 1916, A 216, 393) determined the ratio as 200.288:100. Guye and Pintza (*Mem. Sci.*

Phys. Nat. 1908, 35, 594) showed that 1 volume of nitrogen combines with 3.00172 volumes of hydrogen to form ammonia. These slight differences from whole numbers are due to the different compressibilities of the gases also shown in the deviations from Boyle's law. Gay-Lussac's results were published in 1808, just after the introduction of the atomic theory by Dalton.

It was now evident from the facts (a) that gases combine in simple proportions by volume and (b) that gases combine in simple proportions by atoms, that there must be some simple relationship between the numbers of atoms in equal volumes of gases. Berzelius assumed from this that equal volumes of gases contain equal numbers of atoms. That this was not the case was pointed out by Dalton himself, who showed that the volume changes that should occur on the chemical combinations of gases were not those that were predicted from the above statement of Berzelius. For example, as nitric oxide (NO) is formed by the union of one atom of nitrogen and one of oxygen, we should expect that 1 volume of nitrogen and 1 volume of oxygen would give 1 volume of nitric oxide. It is found that 2 volumes of nitric oxide are produced. Thus, supposing 1 litre of oxygen containing n atoms, combined with an equal volume (1 litre) of nitrogen, which would also contain n atoms, then the 2 litres of nitric oxide, that would be experimentally found to be produced, could only contain n molecules

(compound atoms) of NO or one litre would contain $\frac{n}{2}$ particles—a direct contradiction of the statement that equal volumes of gases contain equal numbers of atoms. Avogadro in 1811 cleared away this and other difficulties in the way of the atomic theory; but his work was overlooked for nearly 50 years, during which time the atomic theory made but little progress, and owing to the uncertainty of determining the chemical formulæ of substances and hence their atomic weights, chemists were thrown back to the use of equivalent weights in their calculations.

AVOGADRO'S HYPOTHESIS

Avogadro assumed that the hypothesis that equal volumes of gases contained equal numbers of particles was correct, but he denied that the particles of elementary gases were necessarily atoms. Avogadro's hypothesis may be stated thus: equal volumes of gases and vapours, under the same conditions of temperature and pressure, contain equal numbers of molecules.

Avogadro pointed out that the *molecules* of elementary gases usually consisted of groups of atoms that moved about and behaved generally as if they were single particles. The definition of atom and molecule must now be restated. The molecule is the smallest mass of a substance that can exist in the free condition. The atom is the smallest particle (mass) of an element that can retain its identity in a chemical change. Both kinds of particle—atom and molecule—had been termed "atom" by Dalton and hence the confusion had arisen. Let us now apply the hypothesis to volume relationship in gaseous combination.

Example.

By experiment:— Hydrogen + chlorine = hydrogen chloride
1 volume + 1 volume 2 volumes.

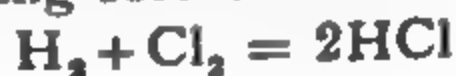
Now, from the statement of Berzelius, that equal volumes of gases contain equal numbers of atoms:—

1 atom	+	1 atom	→	2 atoms
or $\frac{1}{2}$ atom	+	$\frac{1}{2}$ atom	→	1 atom

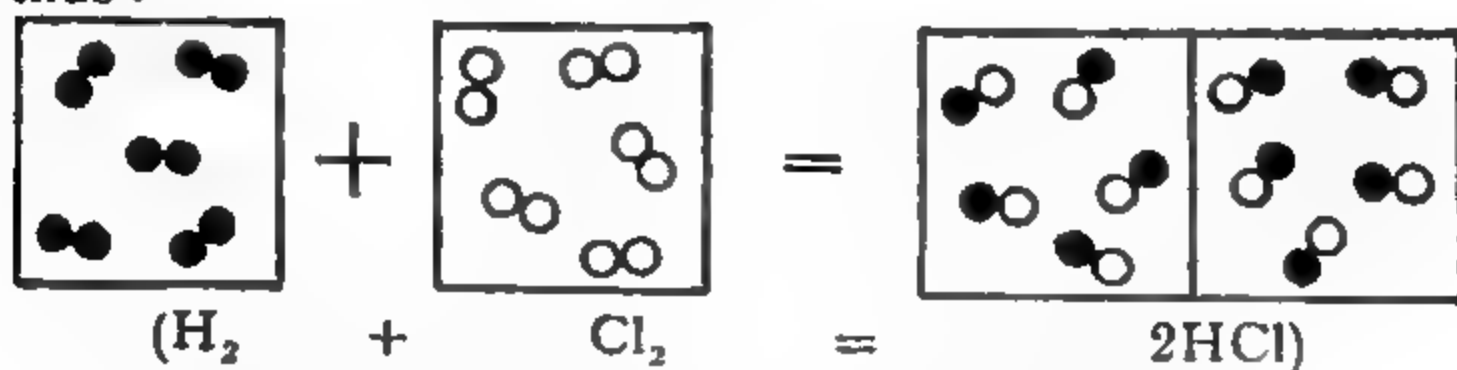
which is contrary to the definition of the atom. But assuming Avogadro's hypothesis to be true and the molecules of chlorine and hydrogen to contain two atoms each:—

1 molecule of hydrogen + 1 molecule of chlorine → 2 molecules of hydrogen chloride.
or 2 atoms of hydrogen + 2 atoms of chlorine → 2 molecules of hydrogen chloride.
or 1 atom of hydrogen + 1 atom of chlorine → 1 molecule of hydrogen chloride.

This reconciles the composition by volume and by atoms and gives the following formula for the reaction:—



The reaction may also be explained diagrammatically thus :—



- represents an atom of hydrogen.
- represents a molecule of hydrogen.
- represents an atom of chlorine.
- represents a molecule of chlorine.
- represents a molecule of hydrogen chloride.

Thus it is to be seen from the diagram that two volumes (1 volume H_2 + 1 volume Cl_2) of the initial gases give rise to two volumes of hydrogen chloride. Also each volume contains an equal number of molecules (in this case 5 for simplicity). It should be noted, too, that the total number of atoms on the left hand side of the equation (20) is the same as the total number of atoms on the right hand side.

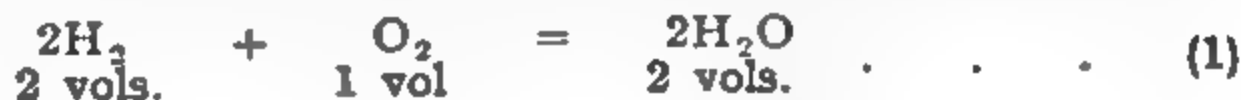
The above reaction can be equally well explained on the assumption that the molecules of hydrogen and chlorine each contain 4, 6, 8 or any other equal even number of atoms. For purposes of simplicity, however, the chlorine and hydrogen molecules are taken to be diatomic and there is ample evidence, both physical and chemical, for the truth of this assumption. Molecules of elements may contain from one to eight atoms in the gaseous state. For example, Hg, He, Na are monatomic, H_2 , O_2 , N_2 , Cl_2 , Br_2 , I_2 , F_2 , are diatomic, O_3 (ozone) is triatomic oxygen, P_4 and As_4 are tetratomic and sulphur may exist as S_8 .

CALCULATIONS INVOLVING THE VOLUMES OF GASES.

Gay-Lussac's law and Avogadro's hypothesis can be applied to the calculation of many chemical problems where the volumes of gases are involved.

Example 1. What volume of air is required for the complete combustion of a mixture of 10 c.c. of hydrogen, 5 c.c. of carbon monoxide (CO) and 30 c.c. of ethylene (C_2H_4)? (Air contains 21% by volume of oxygen.)

In this type of example the full equation for each reaction must first be written down and underneath it, the volume relationships as deduced from Avogadro's hypothesis.



Substitution of the actual quantities of each gas present will now give the volume of oxygen required for the combustion.

Thus : 2 vols. of hydrogen combine with 1 volume of oxygen.

\therefore 10 c.c. of hydrogen combine with 5 c.c. of oxygen.

2 volumes of CO combine with 1 volume of oxygen \therefore 5 c.c. of CO combine with 2.5 c.c. of oxygen.

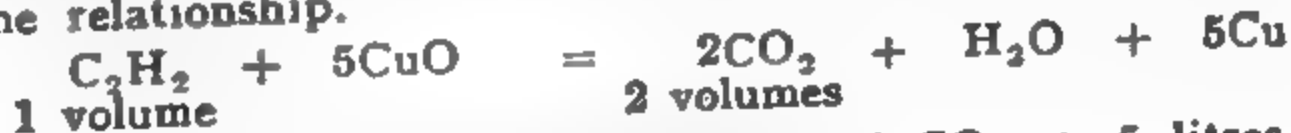
1 volume of C_2H_4 combines with 3 volumes of oxygen \therefore 30 c.c. of C_2H_4 combine with 90 c.c. of oxygen.

The total volume of oxygen for the combustion of all three gases is therefore $5 + 2.5 + 90 = 97.5$ c.c.

$$\begin{aligned} \text{Volume of air required} &= \frac{97.5 \times 100}{21} \text{ c.c.} \\ &= 464.3 \text{ c.c.} \end{aligned}$$

Example 2. What volume of carbon dioxide will be produced on passing 5 litres of acetylene over red hot copper oxide, both gases being measured under the same conditions of temperature and pressure?

Again the equation should first be written, followed by the volume relationship.



1 volume of C_2H_2 produces 2 volumes of CO_2 \therefore 5 litres of C_2H_2 produces 10 litres of CO_2 .

GAS ANALYSIS CALCULATIONS

Similar principles are used in calculating the results of gas analyses. Analysis of mixtures of gases is usually accomplished in the first instance by absorbing various

constituents out of the mixture, one at a time, by the use of reagents, and measuring the diminution in volume of the mixture after treatment with each reagent. The analysis is usually carried out in a gas burette or by one of the many convenient technical processes such as the Orsat method. Usually measurements of volume are made under constant conditions of temperature and pressure and so no corrections for these variables have to be made. The following reagents may be used in the order given; caustic potash solution to absorb carbon dioxide, alkaline pyrogallol or potassium hydrosulphite to absorb oxygen, bromine water to absorb unsaturated hydrocarbons and ammoniacal cuprous chloride solution to absorb carbon monoxide. The remaining gases, which usually contain hydrogen and methane, are estimated by explosion in a eudiometer or an explosion pipette with excess oxygen. The carbon dioxide produced by the combustion of the methane is absorbed in caustic potash, the diminution in volume due to the carbon dioxide being equal to the volume of methane from which it is formed. Any nitrogen that is present is left unchanged after the absorptions and the explosion. For full details of the method of procedure a textbook of quantitative analysis should be consulted.

The following examples illustrate the method of calculating the results.

Example 1. 19.6 c.c. of a mixture of CO_2 , CH_4 and N_2 was analysed as follows. After shaking with caustic potash solution 11.5 c.c. remained. 30 c.c. of oxygen were added and the mixture exploded. After explosion and further treatment with potash solution, 14.4 c.c. of gas remained. Find the volume of each gas present in the mixture.

Treatment with caustic potash solution removed the CO_2 only, \therefore the diminution in volume = the volume of CO_2 .

That is $19.6 - 11.5 = 8.1$ c.c. of CO_2 present.

The residual 11.5 c.c. of gas consists of methane and nitrogen. Let x = the volume of methane $\therefore 11.5 - x$ = volume of nitrogen.



which means that for the combustion of x c.c. of CH_4 , $2x$ c.c. of O_2 are required.

After explosion and absorption of the CO_2 formed, the total remaining gases were: oxygen $30-2x$ c.c.
nitrogen $11.5-x$ c.c.

These two gases together make up the residual volume of 14.4 c.c.

$$30-2x+11.5-x=14.4$$

$$3x=27.1$$

$$x=9.03 \text{ c.c. methane and } 11.5-x=2.47 \text{ c.c. nitrogen.}$$

The mixture therefore contained 8.1 c.c. CO_2 , 9.03 c.c. CH_4 and 2.47 c.c. N_2 .

Example 2. A fuel gas yielded the following analytical data :—

(a) volume of gas used for analysis = 86.3 c.c.

(b) volume after absorption by KOH = 78.6 c.c.

(c) volume after absorption by cuprous chloride = 51.8 c.c.

(d) volume taken from (c) for explosion = 29.1 c.c.

(e) volume of (d) after addition of air = 82.4 c.c.

(f) volume after explosion = 65.0 c.c.

Temperature and pressure remain constant during the analysis.

Calculate the percentage composition of the gas.

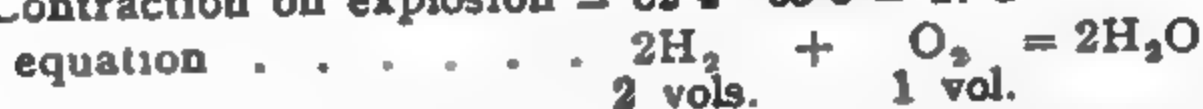
$$\text{CO}_2 \text{ absorbed by the potash} = 86.3 - 78.6 = 7.7 \text{ c.c.}$$

$$\text{hence \% CO}_2 = \frac{7.7}{86.3} \times 100 = 8.9\%$$

$$\text{CO absorbed by cuprous chloride} = 78.6 - 51.8 = 26.8 \text{ c.c.}$$

$$\text{hence \% CO} = \frac{26.8}{86.3} \times 100 = 31.1\%$$

$$\text{Contraction on explosion} = 82.4 - 65.0 = 17.4$$



If the water produced during the explosion is all condensed to liquid; then the contraction will represent the volume of hydrogen exploded + half its volume of oxygen, or $\frac{2}{3}$ of the contraction is due to the hydrogen;

$$\therefore \text{vol. of hydrogen } \frac{2}{3} \times 17.4 = 11.6 \text{ c.c. in } 29.1 \text{ c.c. of gas}$$

$$\text{hence \% H}_2 = \frac{11.6 \times 51.8 \times 100}{29.1 \times 86.3} = 23.9\%$$

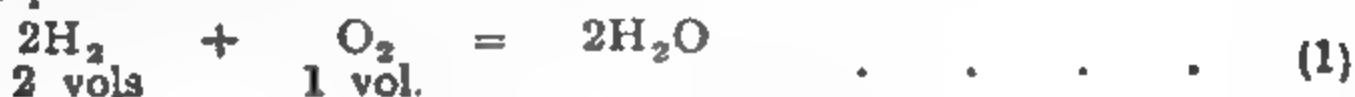
$$\text{By difference the percentage of N}_2 \text{ is } 100 - (8.9 + 31.1 + 23.9) = 36.1\%$$

The % composition is thus

carbon dioxide	= 8.9%
carbon monoxide	= 31.1%
hydrogen	= 23.9%
nitrogen	= 36.1%

Example 3. 50.2 c.c. of a mixture of hydrogen, methane and nitrogen was mixed with 100 c.c. of oxygen and exploded, the volume of the residual gases being 77.2 c.c. After shaking with caustic potash solution 57.8 c.c. remained. Find the volume of each gas in the mixture.

Equations



from equation (2) it is seen that methane produces its own volume of carbon dioxide. The contraction on shaking with caustic potash, due to the absorption of the carbon dioxide, thus represents the volume of methane: $77.2 - 57.8 = 19.4$ c.c.

Volume of hydrogen + nitrogen is thus $50.2 - 19.4 = 30.8$ c.c.

let x = the volume H_2 , then $30.8 - x$ = vol. of N_2 .

On explosion the decrease in volume is due to :—

x c.c. H_2 + $\frac{1}{2}x$ c.c. $O_2 = 1.5x$ c.c. (from equation 1) and only 2×19.4 c.c. O_2 (from equation 2) as methane produces its own volume of CO_2 .

Total contraction is thus $= 1.5x + 38.8 = 150.2 - 77.7 = 73 \text{ c.c.}$

$$1.5x = 34.2$$

$x = 22.6$ c.c. hydrogen

hence $30.8 - 22.8 = 8$ c.c. of nitrogen.

The composition of the mixture is thus :—methane 19·4 c.c.
hydrogen 22·8 c.c.
nitrogen 8·0 c.c.

PROBLEMS INVOLVING GAS VOLUMES AND GAS ANALYSIS

(Answers to those questions with odd numbers will be found at the end of the book)

- 106 A mixture of 10 c.c. of CO , 5 c.c. of CO_2 and 15 c.c. of CH_4 was exploded with 50 c.c. of oxygen. The residual gas was collected over caustic potash solution, all measurements being made at 17°C and 748 mm. pressure. Calculate the volume of the residual gas.
- 107 Calculate the volume of hydrobromic acid formed by the complete decomposition of 2 litres of hydrogen iodide by bromine.
- 108 What volume of oxygen will liberate the same amount of iodine from excess of hydrogen iodide as 1 litre of chlorine?
- 109 How many litres of air (20% oxygen) are required for the combustion of 1 litre each of (1) hydrogen, (2) methane, (3) ethylene and (4) acetylene, all measurements being made at N.T.P.?

- 110 Calculate the minimum supply of air (containing 21% oxygen by volume) necessary for the complete combustion of 15 cu. ft. of gas containing 30% CH_4 , 50% H_2 , 10% CO , 5% CO_2 and 5% N_2 .
- 111 What volume of oxygen is necessary for the combustion of (1) 250 c.c. of carbon disulphide vapour, (2) 500 c.c. of hydrogen iodide, (3) 200 c.c. of hydrogen sulphide and (4) 1 litre of hydrogen, all measurements being made under the same conditions of temperature and pressure?
- 112 150 c.c. of a hydrocarbon C_xH_y were exploded with excess oxygen. How much oxygen was required for the combustion, how much carbon dioxide was produced, and how much carbon monoxide could be produced from it by reduction with carbon?
- 113 A quantity of an unsaturated hydrocarbon of the formula C_3H_4 forms an addition compound, $\text{C}_3\text{H}_6\text{Br}_2$ with 23 c.c. of bromine vapour. What volume of the hydrocarbon was present?
- 114 30 c.c. of methane, CH_4 and ethane C_2H_6 , were exploded with 100 c.c. of oxygen. Potash absorbed all but 10 c.c. of the residual gases, all measurements being made at the same temperature and pressure. What volume of methane and of ethane was there in the mixture?
- 115 1 litre of ammonia gas was decomposed completely by sparking, 2 litres of hydrogen-nitrogen mixture resulting. After addition of excess oxygen the volume was 3200 c.c. After explosion, 950 c.c. of gas remained. Deduce from these data the formula of ammonia.
- 116 A gaseous hydrocarbon contains 82.75% C and 17.25% H. When burnt with a sufficient amount of oxygen, 100 c.c. of the hydrocarbon yield 400 c.c. of CO_2 , both gases being measured under the same conditions of temperature and pressure. Find (a) the empirical and (b) the molecular formula of the hydrocarbon.
- 117 How much oxygen at 18° and 740 mm. would be required for the complete combustion of 100 c.c. of arsine, measured at N.T.P.?
- 118 3 c.c. of a mixture of methane and ethylene were exploded with excess of air. Caustic soda solution absorbed 5 c.c. from the residual gases. Find the proportion of the two gases in the mixture.
- 119 12 c.c. of a mixture of methane and ethylene were exploded with excess of oxygen. Caustic potash absorbed 17 c.c. from the resulting mixture. Find the proportion of the two gases in the mixture.

- 120 15 c.c. of a mixture of hydrogen and methane were exploded with 18 c.c. of oxygen. Caustic potash absorbed all the residual gas. What proportions of hydrogen and methane did the mixture contain?
- 121 20.4 c.c. of a mixture of carbon dioxide, methane and nitrogen was analysed as follows. After shaking with caustic potash solution, 9.0 c.c. remained. 20 c.c. of oxygen were added and the mixture exploded. After explosion and further treatment with caustic potash, 5.9 c.c. remained. What was the volume of each gas present in the mixture?
- 122 What volume of air is required for the complete combustion of a mixture of 10 c.c. of hydrogen, 40 c.c. of acetylene, 5 c.c. of carbon monoxide and 5 c.c. of oxygen? (Air contains 20% oxygen by volume.)
- 123 A sample of 39 c.c. of air from a coal mine and suspected to contain methane, was mixed with 10 c.c. of oxygen and the mixture exploded, 45.2 c.c. remaining after the explosion. After addition of hydrogen, the volume was 85.2 c.c. and on further explosion contracted to 43.2 c.c. Was there any methane in the air? Calculate the percentage composition of the air.
- 124 75 c.c. of oxygen were added to 25 c.c. of a mixture of methane and ethane and the mixed gases exploded. After explosion, caustic potash extracted 31 c.c. from the total volume. Calculate the proportion of the two gases in the mixture and also the volume of oxygen left after the explosion.
- 125 15 c.c. of a certain hydrocarbon were mixed with 100 c.c. of oxygen in a eudiometer. After explosion, potassium hydroxide solution absorbed 45 c.c. of gas from the residue, the remaining 25 c.c. being oxygen. What was the formula of the hydrocarbon?
- 126 What volume of nitric oxide measured at N.T.P. is required to burn 50 c.c. of carbon disulphide vapour measured at 760 mm. and 47°C . and what is the volume of the residual gases at N.T.P.?
- 127 30 c.c. of a methane, acetylene mixture were exploded with 70 c.c. of oxygen over strong caustic potash solution. The residual gases occupied 4.0 c.c. Calculate the percentage composition of the mixture.
- 128 A mixture of 32 c.c. of methane, hydrogen and nitrogen was exploded with 61 c.c. of oxygen. Strong caustic potash solution absorbed 24.1 c.c. from the residual gases which measured 34.5 c.c. before the potash treatment. Find the percentage of the three gases in the mixture.

- 129 36 c.c. of ammonia gas containing some nitrogen were catalytically oxidised by 60 c.c. of oxygen, the nitrogen remaining unchanged. After cooling and waiting until equilibrium had been established, the residual gases occupied 39.5 c.c., all volumes being measured at N.T.P. Calculate the percentage of nitrogen in the ammonia.
- 130 28 c.c. of chlorine monoxide were heated with 60 c.c. of hydrochloric acid gas and the resulting mixture exploded with 60 c.c. of hydrogen. What volume of gas is produced and what volume would be left on washing the mixture with water? All measurements were made at N.T.P.
- 131 100 volumes of an illuminating gas contained 4.72 volumes of olefines (ethylene and propylene) which yielded on combustion 10.98 volumes of carbon dioxide. Calculate the illuminating power of the gas expressed as effective percentage of ethylene.
- 132 An analysis of coal gas was carried out by successive absorptions of carbon dioxide, ethylene, oxygen and carbon monoxide in gas pipettes followed by explosion of the residual gas with an excess of oxygen, and further absorption of carbon dioxide formed. The following results were obtained:—Initial volume of gas 100 c.c.
 Volume after absorption by potash 99.7 c.c.
 Volume after absorption by bromine water 97.3 c.c.
 Volume after absorption by pyrogallol 96.7 c.c.
 Volume after absorption by cuprous chloride 83.6 c.c.
 40 c.c. of the residue were taken and oxygen added until the volume was 100 c.c. After explosion 34.84 c.c. remained and the residual volume after absorption by potash was 20.88 c.c. Calculate the composition of the gas.
- 133 A sample of 100 c.c. of water gas showed a contraction of 7.08 c.c. on bubbling through caustic potash solution. 47 c.c. were now taken from the residue and 43 c.c. of oxygen added, after which the mixture was exploded and the volume found to be 30.8 c.c. Find the percentage of carbon dioxide, carbon monoxide and hydrogen in the gas.
- 134 5 litres of coal gas having the following percentage composition, hydrogen 49.1%, methane 26.2%, carbon monoxide 12.0%, ethylene 4.8%, carbon dioxide 0.7%, oxygen 1.1% and nitrogen 6.1% were passed over red hot copper oxide. What volume of carbon dioxide was produced?
- 135 A sample of 100 c.c. of Mond Gas measured 87.1 c.c. after absorption by caustic potash. After further absorption by cuprous chloride solution the volume became 73.9 c.c. The volume of the mixture was now made up to 100 c.c. by the addition of pure oxygen, and then exploded. The volume was now 57.8 c.c. and after further treatment with caustic potash diminished to 55.5 c.c. Calculate the percentage composition of the gas.

THE RELATIONS BETWEEN THE MOLECULAR WEIGHT AND THE VOLUME OF GASES AND VAPOURS

(1) Relative Density and Molecular Weight.

By definition, the relative density of a gas =

$$\frac{\text{weight of a given volume of gas}}{\text{weight of an equal volume of hydrogen}}$$

Now, by Avogadro's hypothesis, equal volumes of gases contain equal numbers of molecules under the same conditions of temperature and pressure.

$$\begin{aligned}\therefore \text{relative density} &= \frac{\text{weight of one molecule of gas}}{\text{weight of one molecule of hydrogen}} \\ &= \frac{\text{weight of one molecule of gas}}{\text{weight of two atoms of hydrogen}} \\ &= \frac{\text{molecular weight of the gas}}{2.016}\end{aligned}$$

Or if $O = 16$ and $H = 1.008$ are taken as standard of atomic weights, then the molecular weight of a gas = $2.016 \times$ its relative density.

(2) The Molecular Volume.

The molecular weight of any gas = $2.016 \times$ its relative density

$$= 2.016 \times \frac{\text{weight of a given volume of the gas}}{\text{weight of an equal volume of hydrogen}}$$

If, for convenience, we take 2.016 grams as the weight of the hydrogen, the molecular weight will be equal to that weight of gas that occupies the same volume as 2.016 grams of hydrogen. This value is found to be 22.41 litres at N.T.P.

The molecular weight (in grams) of any gas occupies 22.41 litres at 0°C. and 760 mm.

This value, which is strictly exact only for ideal gases and is only approximate for real gases owing to deviations caused by intermolecular attractions, has very wide applications in simplified calculations of the *volumes* of

gases produced by the interaction of known *weights* of materials without involving the densities of the gases concerned. This is done by substituting the gram molecular volume in the equation in place of the gram molecular weight.

Example 1. What volume of oxygen and of hydrogen at N.T.P. will be produced by the electrolysis of 100 gm. of water?

First of all the equation should be written in full.



Then the volume relationships should be expressed.

2 volumes of H_2 + 1 volume of O_2 = 2 gm. molecules of H_2O ,

or 2×22.41 litres H_2 + 22.41 litres O_2 = 2×18 gm. H_2O

22.41 litres of O_2 are produced by 36 gm. of H_2O

$$\therefore \frac{22.41 \times 100}{36} \quad \text{,, , , , , , , } 100 \text{ gm. of } \text{H}_2\text{O} \\ = 62.25 \text{ litres of oxygen}$$

and $62.25 \times 2 = 124.5$ litres of hydrogen are also evolved.

Example 2. 1 gm. of magnesium nitride containing MgO as an impurity, yields 336.15 c.c. of NH_3 at N.T.P. when treated with water. What was the weight of nitride in the mixture?

Equation:— $\text{Mg}_3\text{N}_2 + 3\text{H}_2\text{O} = 3\text{MgO} + 2\text{NH}_3$
(application of mol. wts. and vols.)

100 gm. of Mg_3N_2 evolve 2×22.41 litres of NH_3

$$\therefore \frac{100 \times 336.15}{2 \times 22410} \text{ gm. evolve } 336.15 \text{ c.c. } \text{NH}_3 \\ = 0.75 \text{ gm.}$$

Example 3. Find the percentage composition of an alloy of iron and magnesium, 5 gm. of which, when dissolved in acid, gave 2.81 litres of hydrogen at N.T.P.

Equation:— $\text{Fe} + \text{H}_2\text{SO}_4 = \text{FeSO}_4 + \text{H}_2$
quantitative 56 gm. \rightarrow 22.41 litres
relation:—

Equation:— $\text{Mg} + \text{H}_2\text{SO}_4 = \text{MgSO}_4 + \text{H}_2$
quantitative 24 gm. \rightarrow 22.41 litres
relation:—

Let x = the weight of Fe in 100 gm. of the alloy, then
 $100 - x$ = weight of Mg.

56 gm. Fe give 22.41 litres H_2 ; 24 gm. Mg. give 22.41 litres H_2

$\therefore x$ gm. Fe give $22.41 \times \frac{x}{56}$ litres H_2

and $(100-x)$ gm. Mg. give $22.41 \times \frac{(100-x)}{24}$ litres

Now the H_2 from the iron + H_2 from the magnesium makes up the total volume of gas from 100 gm. of the alloy.

$$= \frac{2.81 \times 100}{5} = 56.2 \text{ litres}$$

$$\therefore 22.41 \times \frac{x}{56} + \frac{22.41 (100-x)}{24} = 56.2$$

$$\text{or } 22.41 \frac{(3x+700-7x)}{168} = 56.2. \quad \therefore 4x = 280 \quad x = 70$$

The alloy therefore contains 70% of iron and 30% magnesium.

PROBLEMS INVOLVING THE USE OF THE GRAM MOLECULAR VOLUME

(Answers to those questions with odd numbers will be found at the end of the book)

- 136 What volume of hydrogen at 15°C . and 770 mm. can be produced by dissolving 70 gm. of pure zinc in sulphuric acid?
- 137 What volume of ammonia gas at N.T.P. is required to neutralise 100 gm. of a 43% solution of hydrochloric acid?
- 138 Determine the volume of sulphuretted hydrogen that could be obtained by reacting on 1 Kgm. of 78% pure iron sulphide with excess of hydrochloric acid.
- 139 What volume of air ($21\%O_2$) at 17°C . and 755 mm. is required to convert 25 gm. of sulphur into sulphur dioxide, and what volume of the dioxide will be obtained at N.T.P.?
- 140 Determine the volume of hydrochloric acid gas at N.T.P. required to precipitate all the silver from a solution containing 3.76 gm. of silver nitrate.
- 141 25 litres of steam, measured at 100°C . and 760 mm. are heated in an iron bomb to 300° under pressure. Calculate the increase in weight of the iron and the volume of hydrogen produced and measured at N.T.P.
- 142 Calculate the volume of nitrous oxide measured at 17°C . and 760 mm. obtained by heating 10 gm. of pure ammonium nitrate.
- 143 What volume of air is required for the complete combustion of 50 Kgm. of coal having the following percentage composition:—C 85.46%, H 7.21%, O 5.37%, the rest being ash?

- 144 50 c.c. of methane measured at 20°C . and 750 mm. were passed over of excess of red hot copper oxide. What was the decrease in weight of the latter?
- 145 What weight of potassium chlorate is required to produce sufficient oxygen to combine with 15 litres of hydrogen at N.T.P.?
- 146 How many cubic centimetres of oxygen at 17°C . and 748 mm. could be obtained by the action of H_2O_2 on 2.5 gm. of potassium permanganate in sulphuric acid solution?
- 147 What volume of gas would be evolved on heating 20 gm. of copper (a) with concentrated sulphuric acid and (b) with dilute nitric acid?
- 148 The gas obtained by heating 17.4 gm. of manganese dioxide with hydrochloric acid was led into excess ammonia solution. What volume of gas was evolved at 17°C . and 720 mm.?
- 149 A manufacturer of bleaching powder requires 100,000 litres of chlorine. How much common salt would he require as a source of his chlorine, allowing for 14% loss during the process?
- 150 What volume of water gas could be obtained by passing 20 Kgm. of steam over incandescent coke, no CO_2 being formed?
- 151 The hydrogen necessary to fill a 25,000 litre balloon was produced by passing steam over red hot scrap iron. How much iron of 85% purity is required, assuming that it is completely converted to the black oxide of iron?
- 152 10 gm. of a compound having the formula $\text{C}_x\text{H}_y\text{N}_z$ were burnt in oxygen. What volume of oxygen was required, and what was the volume and composition of the gaseous products of combustion at N.T.P.?
- 153 25 gm. of a compound having the formula $\text{C}_x\text{H}_y\text{N}_z$ were burnt in oxygen. What volume of oxygen was required, and what was the volume and composition of the gaseous products of combustion, all measurements being made at 0°C . and 750 mm.?
- 154 Write the equation for the preparation of phosphine from phosphorus and caustic soda and calculate the volume of phosphine at N.T.P. that can be obtained from 10 gm. of phosphorus.
- 155 What volume of carbon monoxide measured at N.T.P. could be obtained from (a) 25 gm. of potassium ferrocyanide $\text{K}_4\text{Fe}(\text{CN})_6$, and (b) from 30 gm. of oxalic acid crystals $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ with sufficient amounts of sulphuric acid?
- 156 A sample of anthracite coal has the following percentage composition:—C = 86.4%, volatile matter = 6.2%, moisture = 2.1%, ash = 5.3%. Assuming the volatile matter

to be methane, calculate the volume of air at 750 mm. and 25°C . necessary for the complete combustion of 1 Kilogram of the coal.

- 157 Assuming that 1.1 litres of carbon dioxide are absorbed in sunlight by each square metre of leaf surface per hour; calculate the weight of carbon that will be assimilated by a plantation of 1,000 trees, possessing on an average 100,000 leaves of average area 30 sq. cm., during a summer's day of ten hours' sunlight.
- 158 1.04 gm. of a mixture of anhydrous ammonium nitrate and ammonium nitrite were heated, and the mixed gases evolved found to occupy when dry, 363 c.c. at 18°C . and 720 mm. What was the percentage composition of the mixture?
- 159 1 gram of a mixture of anhydrous sodium chloride, sodium carbonate and potassium nitrate gave off 48.6 c.c. of carbon dioxide at N.T.P. when heated with dilute acid. By the action of concentrated sulphuric acid the whole mixture gave 1.130 gm. of the mixed sulphate. Calculate the percentage of the three salts in the mixture.
- 160 0.85 gm. of the mixed carbonates of barium and magnesium gave, on treatment with hydrochloric acid, 203 c.c. of carbon dioxide at 13°C and 570 mm. Find the proportions of the two carbonates in the mixture.

GAS DENSITIES

The term *density* of a gas or vapour is often incorrectly used to indicate the *relative density* or *specific gravity* of the gas or vapour with reference to hydrogen at the same temperature and pressure. The true density or mass per unit volume obviously depends on the units chosen, but with a unit of volume of half the gram molecular volume, 11.205 litres measured at 0°C . and 760 mm., and a unit of mass of one gram, it becomes numerically equal to the relative density referred to hydrogen. It becomes evident that the density expressed in grams per litre at 0°C . and 760 mm. must be multiplied by 11.205 if it is to be converted to the relative density with respect to hydrogen. Relative densities referred to air as standard must be multiplied by 14.41 to bring them to the relative density referred to hydrogen, as the relative density of air to hydrogen is 14.41.

The deductions from Avogadro's hypothesis on p. 49 that the molecular weight of a gas equals twice (or on

the standard $O = 16$, 2.016 times) its relative density furnishes a valuable method of determining the molecular weights of gases or of substances capable of being vaporised. The relative density will be the weight of 11.20 litres of the gas or vapour at N.T.P., or the molecular weight is the weight of 22.4 litres at N.T.P.

The density of a gas is determined by weighing an evacuated globe, filling it with the gas and re-weighing. The volume of the globe is determined by weighing it full of distilled water.

Example. Find the density of carbon dioxide from the following data :—

Weight of flask evacuated 138.096 gm.

Weight of flask full of CO_2 139.726 gm.

Weight of flask full of water 1028.3 gm.

Temperature of the gas $15^\circ C.$, pressure 748 mm.

Assuming the density of hydrogen to be 0.089 gm. per litre calculate the relative density of carbon dioxide.

Weight of carbon dioxide will equal the weight of the flask full of the gas minus the weight of the evacuated flask.

$$= 139.726 - 138.097$$

$$= 1.629 \text{ gm.}$$

Volume of the flask = volume of water contained in it = $1028.3 - 138.1$

$$= 890.2 \text{ c.c. at } 15^\circ C. \text{ and } 748 \text{ mm.}$$

$$= 890.2 \times \frac{273}{288} \times \frac{748}{760} \text{ c.c. at N.T.P.}$$

$$= 830.7 \text{ c.c.}$$

Density = weight of one litre

$$= 1.961$$

Relative density of carbon dioxide = $\frac{\text{density of carbon dioxide}}{\text{density of hydrogen}}$

$$= \frac{1.961}{0.089}$$

$$= 22.04$$

In accurate work corrections have to be made for the buoyancy of the air, as the true weight of the globe in vacuum will be the apparent weight of the globe in air plus the weight of the displaced air. To eliminate this correc-

tion and also errors due to the variable film of moisture that is condensed on the surface of the globe, a compensating globe may be used. There is still a correction to be applied for the shrinking of the globes under pressure. If allowance is made for all these possible sources of error, accurate results for the densities of gases may be obtained by the method outlined.

VAPOUR DENSITY DETERMINATIONS

As vapours obey, although only approximately, the same laws of expansion as gases, it is possible to reduce the volume of a known weight of vapour that has been determined under definite conditions of temperature and pressure, to N.T.P. and so find the density of the vapour by the same means as that used for gases. Such a density will be a purely hypothetical value as the vapour may exist as a liquid or a solid at 0° and 760 mm., but it is a convenient quantity and divided by the density of hydrogen at N.T.P. gives the (relative) *vapour density*.

Determinations of vapour density are valuable for the calculation of molecular weights and may be carried out of the following methods:—

(I) HOFFMANN'S METHOD

In this method the liquid is weighed into a small stoppered bottle so that it is quite full and no air bubbles are present. The bottle is now placed into a wide barometer tube of about a metre in length, surrounded by a bath of vapour which maintains the temperature constant and considerably above the boiling point of the liquid whose density has to be found. When the bottle reaches the top of the mercury in the barometer tube the stopper is forced out owing to the reduced pressure, and the liquid volatilises. After the mercury level becomes constant, the following data are noted:—

(i) The volume of the vapour in c.c. as read off from the graduated tube.

(ii) The temperature of the jacket.

(iii) The pressure of the vapour, which is approximately given by the barometric pressure minus the height of mercury above the level in the trough.

The weight of the liquid is known and also the volume of its vapour under definite conditions of temperature and pressure, and so the vapour density may be calculated.

Example. 0.285 gm. of chloroform gave 113.4 c.c. of vapour in a Hoffmann's apparatus at 100°C. Barometric pressure 760 mm.; height of mercury above level in bath 271 mm.

$$113.4 \text{ c.c. at } 100^\circ\text{C. and } 760 - 271 \text{ mm.} = 113.4 \times \frac{273}{373} \times \frac{489}{760} \text{ c.c. at N.T.P.} \\ = 53.4 \text{ c.c.}$$

53.4 c.c. is the volume occupied by 0.285 gm. at N.T.P.

$$\therefore 11200 \text{ c.c. would weigh } \frac{0.285 \times 11200}{53.4} = 59.7 \text{ gm.}$$

$$\therefore \text{vapour density} = 59.7$$

(II) DUMAS' METHOD

In this method a glass bulb of capacity about 200 c.c., with a drawn-out neck, is thoroughly cleaned, dried and weighed. Some of the liquid whose vapour density is to be found is now drawn into the bulb by warming it and allowing it to cool with the neck dipping into the liquid. The quantity of liquid introduced should be more than sufficient to fill the bulb when it is vaporised, so as to ensure that all air is expelled.

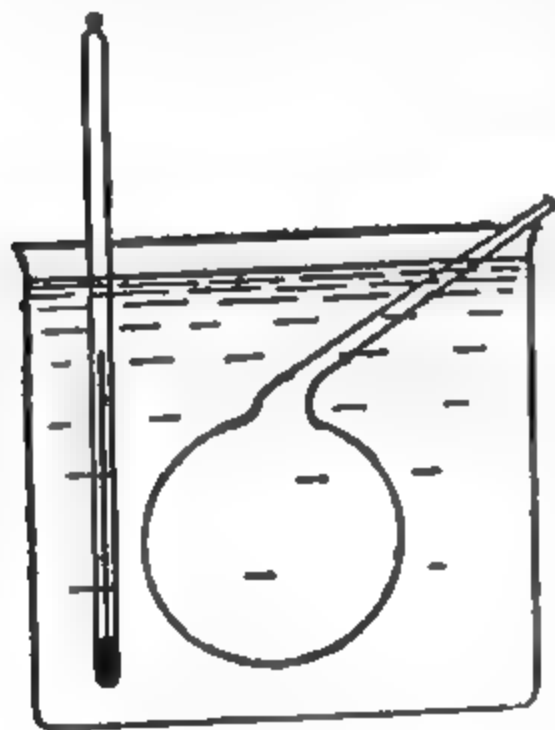


FIG. 3.

The bulb is now placed in an iron bath containing water, oil, paraffin wax or some other substance; the temperature being kept at about 40° above the boiling point of the liquid under investigation. Volatilisation occurs, air being expelled rapidly and the bulb filled with vapour. When the rush of vapour has ceased, the tip of the neck is sealed off and the

temperature of the bath read. The bulb is now removed from the bath, cleaned, dried and weighed. The neck is then scratched with a file and the tip broken under the surface of water that has been boiled free from dissolved gases. Water rushes into the bulb and fills it completely. It is now re-weighed full of water and with the piece of the neck that has been broken off. The atmospheric pressure during the experiment is noted.

Example. The following results were obtained during the determination of the vapour density of an organic compound by Dumas' method.

Weight of bulb filled with air at $16^{\circ}\text{C.} = 27.617 \text{ gm.}$
 " " " " vapour at $162^{\circ}\text{C.} = 27.914 \text{ gm.}$
 " " " " water $= 204.7 \text{ gm.}$

Barometric pressure throughout the experiment $= 760 \text{ mm.}$

Determine the vapour density and hence the molecular weight of the liquid.

Volume of bulb $= 204.7 - 27.6 = 177.1 \text{ c.c.}$

$177.1 \text{ c.c. at } 16^{\circ}\text{C. and } 760 \text{ mm. become } 177.1 \times \frac{273}{289} = 167.3 \text{ c.c.}$
 at N.T.P.

density of air at N.T.P. $= 1.293 \text{ gm. per litre}$

$\therefore 167.3 \text{ c.c. of air weigh } \frac{1.293 \times 167.3}{1000} \text{ gm.}$
 $= 0.216 \text{ gm.}$

Then weight of bulb, vacuum $= 27.617 - 0.216 \text{ gm.} = 27.401 \text{ gm.}$
 weight of vapour $= 27.914 - 27.401 = 0.513 \text{ gm.}$

Volume of vapour $= 177.1 \text{ c.c. at } 162^{\circ}\text{C. and } 760 \text{ mm.}$

$= 177.1 \times \frac{273}{435} = 111.1 \text{ c.c. at N.T.P.}$

The vapour density will be the weight that occupies 11.2 litres
 $111.1 \text{ c.c. of the vapour weigh } 0.513 \text{ gm.}$

$11.2 \text{ litres " " " } \frac{0.513 \times 11200}{111.1} = 51.7 \text{ gm.}$

$\therefore \text{vapour density} = 51.7$

Molecular weight $= \text{vapour density} \times 2 = 51.7 \times 2$
 $= 103.4$

This method is of much wider application than that of Hoffmann, but is not so accurate and has the disadvantage of requiring a comparatively large amount of liquid for a single determination; also if the substance

contains any high boiling impurities these come off last and the observed density is too high. Dumas' method has been extended to the determination of vapour densities at high temperatures, a porcelain bulb being used in a bath of sulphur or a conveniently melting metal. Often the weight of vapour in the bulb is determined by a chemical analysis of the contents.

(III) VICTOR MEYER'S METHOD

Victor Meyer's displacement method is the converse of Dumas' method, in that the volume of vapour due to the volatilisation of a given weight of liquid or solid is measured, instead of the weight of a fixed volume of vapour.

The heat necessary for the vaporisation of the substance is provided by the bath A, which contains a liquid boiling some 30-40° above the boiling point of the liquid under investigation, but whose temperature need not be accurately known. In the bath is the bulb B, in which the vaporisation actually takes place. It is connected to a gas burette, F, by means of a capillary-tube connection and the three-way tap H. In carrying out a determination, the liquid in the bath A is first allowed to boil gently with the tap (H) open to the air for some 15 minutes, by which time heat equilibrium should be established. A

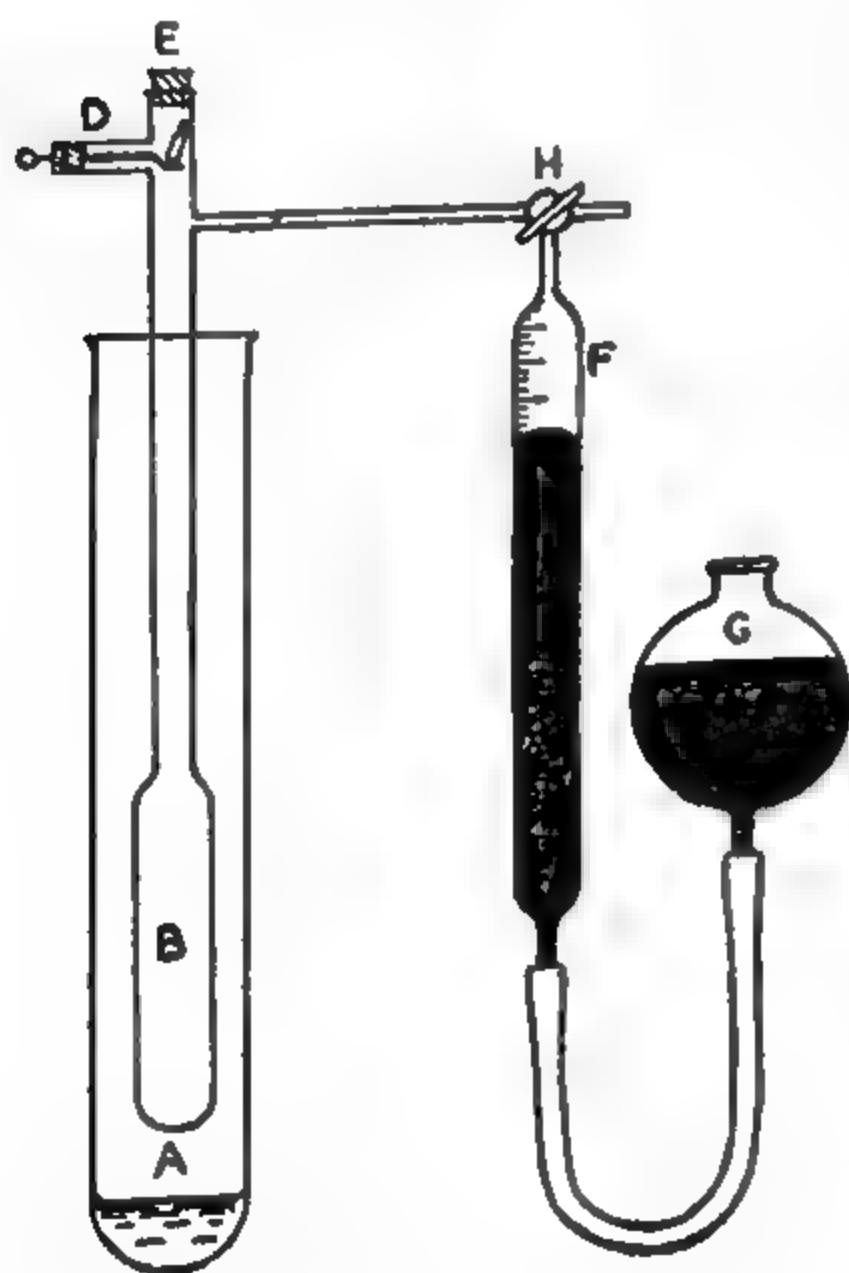


FIG. 4.

weighed amount of the substance contained in a small stoppered bottle is now introduced into the apparatus at E and the cork quickly replaced. The bottle falls on to the glass rod at D. Connection is now made between the vaporisation tube and the gas burette which is full of water or mercury, by means of the tap H, after which D is pulled out and the bottle falls to the bottom of the bulb B, which is prevented from breaking by a little asbestos on the bottom. The liquid vaporises quickly and the stopper is blown out of the bottle. The vapour displaces the air from the bulb B into the burette F, where its volume is read after it becomes constant, the level T being made the same as that in the reservoir G. The volume of the vapour is equal to the volume of the air displaced, and this volume is known under definite conditions of temperature and pressure, and so the vapour density may be calculated. If the gas is collected over water allowance must be made for the pressure of water vapour in the gas burette.

Example. 0.1462 gm. of a liquid expelled 31.2 c.c. of moist air at 15°C. and 760 mm. when vaporised in a Victor Meyer's apparatus. Calculate the molecular weight of the liquid. (Vapour pressure of water at 15° = 13 mm.)

$$\text{Volume of dry air expelled at N.T.P. will be } 31.2 \times \frac{273}{288} \times \frac{760-13}{760} = 29.07 \text{ c.c.}$$

This equals the volume of vapour, reduced to N.T.P.

Now 29.07 c.c. of vapour weigh 0.1426 gm.

$$\therefore 22.4 \text{ litres " " " } \frac{0.1426 \times 22410}{29.07} = 109.9 \text{ gm.}$$

The molecular weight of the substance is 109.9

(The molecular weight may also be found from a direct calculation of the vapour density, as follows:—

From the calculation above, the volume of vapour at N.T.P. = 29.07 c.c.

$$\text{vapour density} = \frac{\text{weight of vapour}}{\text{weight of an equal volume of hydrogen}} \\ (\text{density of hydrogen} = 0.000089 \text{ gm. per c.c.})$$

$$\therefore \text{vapour density} = \frac{0.142}{0.000089 \times 29.07} = 55.0$$

$$\text{Molecular weight} = 55.0 \times 2 = 110.0$$

This method of calculation is longer and is not recommended.)

Victor Meyer's method for the determination of vapour densities is accurate to within 2.5% only, but it is much more convenient, requires a much smaller quantity of the material and is more frequently used than Dumas' method. Victor Meyer's method was applied by Nernst (*Z. Electrochem.*, 1903, 9, 622) to the determination of vapour densities at high temperatures, using an iridium bulb which could be heated electrically to 2000°C.

DETERMINATION OF THE FORMULÆ OF GASES

The formula of a gas or of a substance capable of being vaporised is usually deduced from its molecular weight (as calculated from its relative density) and from the volume relationships that hold in one or more of its reactions.

Example. *Determination of the formula of ammonia gas.* A long tube, fitted with a tap at the top, was filled with chlorine gas and concentrated ammonia solution added drop by drop. Each drop of ammonia reacted with a yellowish flame and the formation of white clouds of ammonium chloride, which were washed down with a little water at the end of the reaction and sulphuric acid added to neutralise the excess ammonia solution that had been added. The tube was then cooled and connected to a beaker of boiled-out water. On opening the tap at the top of the tube, water flowed in. It was found that the residual nitrogen filled one-third of the tube. The relative density of ammonia was found to be 8.5. Find the formula of the gas.

Molecular weight = $2 \times \text{the relative density} = 8.5 \times 2 = 17$.

Now three volumes of chlorine react with the hydrogen of ammonia to form hydrogen chloride and leave 1 volume of nitrogen.



\therefore the three volumes of chlorine were equivalent to three volumes of hydrogen, *i.e.*, 1 volume of nitrogen is combined in ammonia, with three volumes of hydrogen. \therefore the formula is $(\text{NH}_3)_x$.

Now the sum of the constituent atomic weights will be equal to the molecular weight, which is known.

$$\begin{aligned} \text{or } (14+3) \times x &= 17 \\ x &= 1 \end{aligned}$$

and so the formula must be NH_3 .

PROBLEMS ON THE DETERMINATION OF VAPOUR DENSITIES, MOLECULAR WEIGHTS AND THE FORMULÆ OF GASES

(Answers to those questions with odd numbers will be found at the end of the book)

161 The normal densities of the three inert gases, helium, neon and argon are 0.1786, 0.9002 and 1.7838 respectively, find their relative densities and, assuming them to be monatomic, their atomic weights.

162 The densities of a number of gases are given below. Calculate the molecular weights of these gases:—

nitrous oxide	1.9777 gm./litre
nitric oxide	1.3402 gm./litre
ammonia	0.7708 gm./litre
sulphur dioxide	2.9267 gm./litre
methane	0.7168 gm./litre
hydrogen chloride	1.6392 gm./litre

163 The following results were obtained in the determination of the density of nitrogen by the method of compensating globes:—

weight of globe evacuated = 0.000 (exactly compensated).

weight of globe full of nitrogen = 53.853 gm.

The pressure during this weighing was 760 mm. and the globes were immersed in ice.

Weight of the globe full of water at 4° = 43,062.4 gm.

Find the normal density and the relative density of nitrogen.

164 The density of sulphur dioxide was determined by weighing a flask full of air, full of sulphur dioxide and then estimating the weight of the gas by chemical means. The following results were obtained:—

Weight of the flask+air = 265.410 gm.

weight of the flask+sulphur dioxide = 269.504 gm.

weight of the sulphur dioxide = 7.335 gm.

All measurements were made at N.T.P. Find the normal density and the molecular weight of the gas.

165 The following data were obtained in two determinations of the vapour density of phosphorous oxide by Hoffmann's method:—

	I	II
weight of material	0.0880 gm.	0.0880 gm.
temperature of tube	160°C.	185°C.
barometric pressure	767 mm.	767 mm.
height of mercury column	612 mm.	601 mm.
volume of vapour	69.7 c.c.	70.7 c.c.

Determine the molecular weight of the oxide and, assuming its empirical formula to be P_2O_3 , find its molecular formula.

- 166 Calculate the molecular weight of camphor vapour from the following data obtained in a determination by Dumas' method:—

weight of bulb+air = 65.526 gm.

weight of bulb+camphor vapour = 66.400 gm.

Temperature of bath $248^{\circ}\text{C}.$, pressure 745 mm. Volume of mercury required to fill the bulb 397 c.c.

- 167 Calculate the molecular weight of alcohol from the following data from a Dumas' determination:—

weight of bulb+air = 47.683 gm.

weight of bulb+vapour = 47.507 gm.

volume of bulb = 326 c.c.

Temperature of sealing, 150° , temperature of weighing, $16^{\circ}\text{C}.$, pressure, 740 mm.

- 168 The molecular weight of aluminium chloride was obtained by a modification of Dumas' method at $400^{\circ}\text{C}.$ The pressure of the vapour was exactly atmospheric, but a small amount of air was present, afterwards found to occupy 242 c.c. at 12 mm. pressure and $16^{\circ}\text{C}.$ The weight of the bulb filled with air was 47.612 gm., and filled with the vapour was 48.586 gm. All weighings were carried out at $16^{\circ}\text{C}.$ and 750 mm. The volume of the bulb was 250 c.c. Calculate the molecular weight of aluminium chloride.

- 169 Calculate the molecular weight of a substance that gave the following data in a vapour density determination by Victor Meyer's method:—Weight of substance taken 0.0619 gm.; volume of air displaced 20.51 c.c., temperature $16.5^{\circ}\text{C}.$, pressure 718 mm. (aqueous tension at 16.5° , 14.00 mm.).

- 170 0.1361 gm. of mercury on vaporisation in Victor Meyer's apparatus displaced a volume of air which measured 17.3 c.c. at $18^{\circ}\text{C}.$ and 745 mm. Calculate the molecular weight of mercury. (Vapour pressure of water at $18^{\circ}\text{C}.$ is 15.5 mm.)

- 171 0.1321 gm. of a certain liquid was vaporised in a Victor Meyer apparatus. The volume of gas expelled and collected over water at $18^{\circ}\text{C}.$ was 31.3 c.c. at 748.9 mm. (Vapour pressure of water at $18^{\circ}\text{C}.$ is 15.5 mm.)

- 172 Vapour density determination on an organic liquid of Victor Meyer's method (accuracy $2\frac{1}{2}\%$) at $150^{\circ}\text{C}.$ and at $250^{\circ}\text{C}.$ gave the following data:—

	I ($150^{\circ}\text{C}.$)	II ($250^{\circ}\text{C}.$)
weight of material taken	0.0884 gm.	0.0622 gm.
volume of air displaced	24.6 c.c.	17.3 c.c.
temperature of water	$16^{\circ}\text{C}.$	$16^{\circ}\text{C}.$
barometric pressure	771 mm.	771 mm.

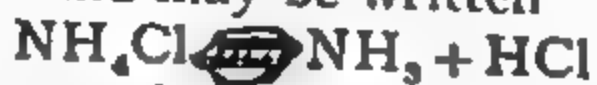
What are the mol. wts. of the vapour at these temperatures, and is there any evidence for the existence of a polymer at the higher temperature? (V.P. of water vapour at 16° , 13.5.)

- 173 An oxide of nitrogen was analysed by burning a spiral of iron wire in it, when the oxygen was removed and half its volume of nitrogen left. The vapour density of the gas was 15, determine its formula.
- 174 The vapour density of the hydride of an element X is 39.0 and on heating, the volume of the gas increases by half. Using the atomic weight tables, identify X and find the formula of its hydride.
- 175 Three hydrides of silicon have vapour densities 16, 31.7 and 46.4 respectively. On heating they all decompose, depositing silicon and producing hydrogen; the first yields twice its volume of hydrogen, the second three times its volume and the third four times. Find the formula of the three gases.

ABNORMAL VAPOUR DENSITIES

When ammonium chloride is vaporised by heating and its vapour density found, a value of 26.75 is obtained for the molecular weight, instead of 53.3 corresponding to the simplest formula, NH_4Cl . On examining the vapour, however, it is found to consist, not of ammonium chloride, but of ammonia gas and hydrochloric acid gas. That this is the case to a small extent at least, may be shown by heating ammonium chloride in a tube with a porous plug in it (Pebal, *Lieb. Ann.*, 1862, 123, 199). The ammonia, being lighter than the hydrochloric acid, diffuses more rapidly through the plug than the hydrochloric acid, and consequently a piece of red litmus paper on the other side of the porous plug from the heated ammonium chloride will turn blue owing to the presence of an excess of ammonia, whereas a piece of blue litmus paper placed actually in the heated vapour, will turn red owing to a residual excess of hydrochloric acid.

On allowing the vapour to cool, the two gases recombine to form ammonium chloride once more. This is a reversible reaction and may be written



If the vapour consisted of ammonium chloride only, then 53.5 gm. of ammonium chloride would occupy 22.4 litres. As, however, the vapour consists entirely of $\text{NH}_3 + \text{HCl}$, and 17 gm. of ammonia occupy 22.4 litres and 36.5 gm. of hydrochloric acid occupy 22.4 litres, there is

present 53.5 gm. of the gaseous mixture in a volume of 44.8 litres. Thus 22.4 litres of the mixture of gases would weigh 26.75 gm, the vapour having an apparent molecular weight of 26.75. Now this is the value obtained from a determination of the vapour density of ammonium chloride. The seemingly abnormal vapour density of ammonium chloride is thus explained by assuming that the salt is completely split up or *dissociated* on vaporisation. It was shown by H. B. Baker that, if the ammonium chloride was carefully dried so as to remove the last traces of moisture, dissociation was prevented and the vapour gave a normal value for its relative density corresponding to a molecular weight of 53.5.

Many examples of dissociation are known; an interesting example being that of hydrogen iodide gas.



The undissociated gas is colourless, but on heating the violet colour of iodine appears and becomes more intense on raising the temperature, while the colour becomes weaker on cooling again.

The degree of dissociation of a vapour, or the fraction of the total number of molecules dissociated under the given conditions, may be deduced in many cases from the vapour density of the substance under these conditions.

This method is not, however, applicable where there is no change in volume on dissociation. In these cases other methods have to be used, such, for example, as a colorimetric estimation of the iodine liberated on the dissociation of hydrogen iodide mentioned above. The calculation of the degree of dissociation may be made as follows. Suppose that there are N molecules present, that the degree of dissociation is α and that each molecule breaks up into x molecules on dissociation.

$1 - \alpha$ will be the proportion of undissociated molecules, and $N(1 - \alpha)$ the total number of undissociated molecules, also $N\alpha x$ will be the number of molecules produced by dissociation. The total number of molecules before dissociation was N , and after dissociation

$$N(1 - \alpha) + N\alpha x = N[1 + \alpha(x - 1)]$$

From Avogadro's hypothesis:

$$\frac{\text{Volume after dissociation}}{\text{Volume before dissociation}} = \frac{N[1 + a(x-1)]}{N}$$

The vapour densities are inversely proportional to the volumes. So if d is the vapour density of the undissociated substance, and Δ the observed vapour density, then

$$\frac{N[1 + a(x-1)]}{N} = \frac{d}{\Delta}$$

$$\text{or } d = \Delta[1 + a(x-1)]$$

$$\therefore a = \frac{d - \Delta}{\Delta(x-1)}$$

if the density D corresponds to complete dissociation,

$D = \frac{d}{x}$; also in the case of ammonium chloride and many

other cases where $x = 2$, $a = \frac{d - \Delta}{\Delta}$ and on complete dis-

sociation, $D = \frac{d}{2}$ or the observed density is equal to half

the density of the undissociated material which, as we have seen, is found experimentally. Similar reasoning enables us to make a quantitative study of association, or the production of more complicated, from simpler molecules.

Example. The following values were obtained for the vapour density of phosphorus pentachloride at various temperatures.

Temperature	Vapour density
182°	73.4
200°	70.0
250°	57.6
300°	52.7

Calculate the degree of dissociation at these temperatures.

The dissociation may be represented by $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$.

The vapour density of the undissociated material will be

$$\frac{(31 + 5 \times 35.5)}{2.016} = 104.12. \quad \text{Let } a \text{ be the degree of dissociation, then}$$

$1 - a$ will be the proportion of undissociated molecules, and as 2 molecules are produced on the dissociation of each molecule of PCl_5 , $2a$ will be the proportion of molecules formed on dissociation.

Now, by Avogadro's hypothesis, the numbers of molecules present before and after the dissociation will be proportional to the volumes of gases before and after the dissociation and hence inversely proportional to the vapour densities before and after dissociation.

$$\therefore \frac{2a+1-a}{1} = \frac{104.12}{\Delta}$$

$$a = \frac{104.12}{\Delta} - 1$$

Taking the values of given above

at 182°	$a = \frac{104.12}{73.4} - 1$	$= .41$
at 200°	$a = \frac{104.12}{70.0} - 1$	$= .49$
at 250°	$a = \frac{104.12}{57.6} - 1$	$= .81$
at 300°	$a = \frac{104.12}{52.7} - 1$	$= .97$

PROBLEMS ON THE DEGREE OF DISSOCIATION OF GASES

(Answers to those questions with odd numbers will be found at end of the book)

(These should be worked out from first principles as in the example above and not from the general formula.)

- 176 Acetic acid has the empirical formula $C_2H_4O_2$ and at 250°C. and 760 mm. it has a vapour density of 29. At 125° the vapour density is 44.5. What information do these figures give as to the state of the molecules of acetic acid in the vapour?
- 177 The thermal dissociation of phosphorus pentabromide was investigated by a colorimetric study of the products of reaction. At a high temperature the colour intensity reached a maximum and a further rise in temperature had no effect. Calculate the vapour density of phosphorus pentabromide at that point.
- 178 Amylene hydrobromide, $C_5H_{11}Br$, has a vapour density of 41.5 at 340°. Calculate the degree of dissociation into amylenes and hydrogen bromide at that temperature.
- 179 The vapour density of ammonium carbamate $CO(NH_2)ONH_2$ is 13. Calculate its degree of dissociation into $2NH_3$ and CO_2 .

180 The relative density of silver vapour at 1000° is 54; that of antimony at 1640° is 140 and that of bismuth at 1700° is 158. Find the atomicity of each element, and if this is fractional calculate the amounts of the two molecular forms present.

181 Iodine molecules, although diatomic at low temperatures, dissociate gradually on raising the temperature, eventually becoming monatomic. The densities at various temperatures are :—

at 600°	125.5
at 1030°	98.3
at 1390°	75.3
at 1500°	64.8

Determine the degree of dissociation of iodine at these temperatures and draw a graph to illustrate the dependence of degree of dissociation on temperature.

182 The vapour density of mercuric sulphide is 77 at 1560° . What is the degree of dissociation, assuming sulphur to exist entirely at S_2 at that temperature? At 670° the vapour density is 85. What reason could you suggest to account for this value?

183 At 400° sulphur trioxide is decomposed to the extent of 2% to form the dioxide; at 700° 40% is decomposed. Calculate the vapour densities of pure sulphur trioxide, the 400° product, the 700° product, and pure sulphur dioxide.

184 The following table gives the relative densities of nitrogen peroxide at various temperatures. Calculate the degree of dissociation in each case and plot a graph to show its dependence on temperature.

T	Δ
26.7°	38.3
60.2°	30.1
100.1°	24.3
135.0°	23.1
140.0°	22.96

185 An oxygen-ozone mixture had the relative density 17.42. Find the percentage of ozone: also what would be the relative density of a mixture containing 30% of ozone?

DIFFUSION OF GASES

It is a common observation that hydrogen diffuses out of an open, inverted jar in opposition to gravity and that air enters. In 1833 Döbereiner noticed a similar phenomenon when he observed that hydrogen stored over water in a cracked flask escaped into the air, the level of water rising in the flask. Graham showed that this was due to the hydrogen diffusing out through the crack

more quickly than air diffused in. He devised an apparatus for the measurement of the rates of diffusion of gases by means of a glass tube, closed at one end by a thin plug of plaster of Paris. The tube was filled with mercury, which was displaced by hydrogen whose volume could be measured by the graduations on the tube. The level of the mercury rose in the tube and eventually reached an equilibrium when it was found that the tube contained only air. At equilibrium then, all the hydrogen had diffused out and been replaced by air, and the final volume gave the volume of air that had diffused out in the same time as the original volume of hydrogen had diffused out. The ratio of these volumes was thus the ratio of the rates of diffusion of hydrogen and air. Graham measured the rates of diffusion of many gases by means of this apparatus and he found that when he allowed gases that were heavier than air to diffuse out of his tube into the air the level of the mercury fell; in other words, gases heavier than air have smaller rates of diffusion than air. From his experimental results Graham deduced his law which states that the rate of diffusion of a gas is inversely proportional to the square root of its relative density.

$$R_1 : R_2 = \sqrt{d_2} : \sqrt{d_1}$$

This relation is an agreement with the kinetic theory of gases, since the rate at which gases will pass through the narrow pores of the plug will be proportional to the mean velocities v_1 and v_2 of their molecules. If two gases are at the same temperature it is assumed that their kinetic energies are identical, $M_1 v_1^2 = M_2 v_2^2$, where M_1 and M_2 are the molecular weights of the gases,

$$\text{hence } M_1 R_1^2 = M_2 R_2^2$$

Now, as the molecular weight of the gas is proportional to its density,

$$d_1 R_1^2 = d_2 R_2^2$$

$$\text{or } R_1 : R_2 = \sqrt{d_2} : \sqrt{d_1}$$

The process of diffusion has been used widely by chemists. Ramsay and Travers (*Proc. Roy. Soc.* 1898, 52, 316) used it to separate helium from the other gases of

cleveite; Soret (*Ann. Chim. Phys.* 1868, 13, 257) used a diffusion method to determine the formula of ozone and Pebal (see p. 63) used it to demonstrate the nature of vaporised ammonium chloride.

The following examples serve to illustrate the methods of calculation of results of diffusion experiments.

Example 1. 100 c.c. of hydrogen were confined in a diffusion tube exposed to the air and at equilibrium a volume of 26.1 c.c. of gas was measured. 100 c.c. of carbon dioxide were now placed in this same tube and when the level of mercury became constant the volume was 123 c.c. Find the molecular weight of carbon dioxide.

100 c.c. of hydrogen diffused out in the same time as 26.1 c.c. of air diffused in,

$$\therefore \frac{\text{rate of diffusion of hydrogen}}{\text{rate of diffusion of air}} = \frac{100}{26.1}$$

$$\text{similarly } \frac{\text{rate of diffusion of carbon dioxide}}{\text{rate of diffusion of air}} = \frac{100}{123}$$

$$\therefore \frac{\text{rate of diffusion of carbon dioxide}}{\text{rate of diffusion of hydrogen}} = \frac{26.1}{123}$$

By Graham's law, rate of diffusion $\propto \sqrt{\text{density}}$

$$\frac{\text{density of carbon dioxide}}{\text{density of hydrogen}} = \frac{123^2}{26.1^2} = \frac{15129}{681.2}$$

$$\frac{21.9}{1}$$

the relative density of carbon dioxide = 21.9

$$\begin{aligned} \text{Molecular weight of carbon dioxide} &= \text{relative density} \times 2.016 \\ &= 21.9 \times 2.016 = 44.1 \end{aligned}$$

Example 2. 100 c.c. of hydrogen were enclosed in a diffusion apparatus exposed to pure oxygen. What volume of gas was left in the apparatus when change in volume was complete?

By Graham's law,

$$\frac{\text{rate of diffusion of hydrogen}}{\text{rate of diffusion of oxygen}} = \frac{\sqrt{\text{density of oxygen}}}{\sqrt{\text{density of hydrogen}}}$$

$$= \frac{\sqrt{16}}{\sqrt{1}} = \frac{4}{1}$$

Thus hydrogen diffuses 4 times as quickly as oxygen, so that while 100 c.c. of hydrogen diffuse out, 25 c.c. of oxygen diffuse in.

PROBLEMS ON THE DIFFUSION OF GASES

(Answers to those questions with odd numbers will be found at the end of the book)

- 186 The rates of diffusion of oxygen and hydrogen are 0.95 and 3.83 respectively compared to the rate of diffusion of air. The normal density of air is 1.293. Find the densities of oxygen and hydrogen.
- 187 The rate of diffusion of methane is 1.34 times that of the air. The density of air is 1.293 and that of hydrogen is 0.089. Determine the molecular weight of methane.
- 188 Hydrogen iodide has the molecular formula HI and hydrogen, H_2 . What are the relative rates of diffusion of these two gases?
- 189 The relative densities of ammonia and carbon dioxide are 8.5 and 22 respectively. What are the relative rates of diffusion of the two gases?
- 190 100 c.c. of oxygen diffuse through a porous vessel in a certain time; what volume of carbon monoxide would diffuse through in the same time?
- 191 If 10 c.c. of methane diffuse through compressed graphite in three minutes, how long will it take (a) 25 c.c. of ethylene and (b) 20 c.c. of acetylene to diffuse?
- 192 Taking the rate of diffusion of hydrogen as unity calculate the rates of diffusion of nitrous oxide, nitric oxide and nitrogen peroxide?
- 193 The rates of diffusion of a series of gases with respect to air are given below: use these data to confirm Graham's law.
- | Gas | Velocity of diffusion |
|----------------|-----------------------|
| hydrogen | 3.83 |
| methane | 1.34 |
| nitrogen | 1.014 |
| oxygen | 0.950 |
| carbon dioxide | 0.812 |
- 194 100 c.c. of hydrogen sulphide were allowed to diffuse out of a diffusion tube into pure oxygen. When equilibrium was established 103.0 c.c. of gas remained in the tube. Using 100 c.c. of hydrogen selenide 159.1 c.c. remained; using 100 c.c. of hydrogen telluride 201.0 c.c. remained. The formulæ of the three gases are H_2S , H_2Se and H_2Te : calculate the atomic weights of sulphur, selenium and tellurium.
- 195 It was found that 67 c.c. of sulphur dioxide diffused in 5½ minutes while under the same conditions 66.8 c.c. of sulphuretted hydrogen diffused in 4 minutes. What is the ratio of the densities of these two gases?

- 196 In experiments made by Soret on the density of ozone by the diffusion of oxygen-ozone, oxygen-chlorine and oxygen-carbon dioxide mixtures, the relative rates of diffusion of chlorine, ozone and carbon dioxide were found to be 0.227 : 0.271 : 0.290. Assuming the relative density of chlorine to be 35.4 and that of carbon dioxide to be 22, find the relative density and the molecular weight of ozone.
- 197 Perkins found that the relative rates of diffusion of mercury and radium emanation were 1 : 1.082. The atomic weight of mercury is 200.6 and it is monatomic in the vaporised condition. Calculate the molecular weight of radium emanation.
- 198 A liquid hydrocarbon had the percentage composition C 83.7%, H 16.3%. 100 c.c. of the vapour of the hydrocarbon were placed in a heated diffusion tube exposed to oxygen. On equilibrium being attained there were 164 c.c. of gas in the tube. What is the formula of the hydrocarbon?
- 199 A certain compound has the percentage composition C 53.33%, H 15.55%, N 31.11 %. 100 c.c. of this same gaseous compound, when placed in a diffusion apparatus exposed to the air, diminished in volume to 79.8 c.c. at equilibrium. Find the molecular formula of the compound.
- 200 Two hydrides of silicon are found to have relative rates of diffusion 1 : 1.39. The lighter gas when passed through a red hot tube deposited 87.6% of its weight as silicon and 100 c.c. of the hydride yielded 200 c.c. of hydrogen. Determine the molecular weights of the two gases.
- 201 A gaseous organic compound contains 38.71% C, 16.13% H and 45.16% N. Its rate of diffusion is 0.254 times that of hydrogen. What is the molecular formula of the compound?
- 202 The relative rates of diffusion of arsenic and xenon are .360 : .387. Xenon is known to be a monatomic gas. What is the atomicity of arsenic?
- 203 Sulphur vapour at 500° diffuses at .577 times the rate of sulphur dioxide at the same temperature. At 860° it diffuses at the same rate as the dioxide. Assuming sulphur dioxide to exist as SO_2 at both these temperatures, determine the molecular weight and formula of sulphur under both these conditions.
- 204 100 c.c. of nitrogen peroxide were placed in a diffusion apparatus surrounded by a steam jacket and exposed to the air. At equilibrium it was found that there were 130 c.c. of air in the tube; calculate the degree of dissociation of N_2O_4 at 100°C.

- 205 50 c.c. of sulphur trioxide were placed in a diffusion apparatus heated to 700° and open to the air. At equilibrium 75.75 c.c. of air were in the tube. Determine the composition of the equilibrium mixture of $2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$ at this temperature.

CHAPTER IV.

ATOMIC WEIGHTS

ATOMIC WEIGHT, EQUIVALENT AND VALENCY

As has been discussed in Chapter II, it is an essential feature of the atomic theory that the atoms of any one element are equal in weight and characterised by that weight. The *atomic weight* of an element is not, in general, the same as its *equivalent weight*—as follows from the fact, expressed by the law of multiple proportions, that one atom of an element *A* may combine with two or more atoms of an element *B*. Since, however, elements unite in simple proportions by atoms, it follows that the atomic weight and equivalent of an element are connected by the relationship:—

$$\frac{\text{Atomic Weight}}{\text{Equivalent Weight}} = \text{a whole number, termed the valency.}$$

Further, in the case of hydrogen, the equivalent weight is the same as the atomic weight (1.008), i.e., the valency of hydrogen = 1. Hence, for other elements, the valency is equal to the number of hydrogen atoms combined with (or replaced by) one atom of the element.

Thus, in arsine AsH_3 , 1 atom of arsenic is combined with 3 atoms of hydrogen.

\therefore valency of arsenic is 3.

Example. What is the valency of phosphorus in phosphorus pentoxide, P_2O_5 ?

Since 1 atom of oxygen unites with 2 atoms hydrogen (forming H_2O).

\therefore valency of oxygen = 2

2 atoms of phosphorus combine with 5 atoms of oxygen, which are equivalent to 10 atoms of hydrogen.

\therefore valency of phosphorus = 5.

An element may exhibit more than one stage of valency. Thus iron has a valency of two in ferrous salts (*e.g.*, FeCl_2), the equivalent being 27.92, and a valency of three in ferric salts (*e.g.*, FeCl_3), the equivalent being 18.61. As the elements are classified in the Periodic Table (*q.v.*), the number of the group in which an element occurs gives at once the highest valency shown by the element—that exhibited in its highest oxide or fluoride. Thus sulphur, in Group VI, shows its highest valency, six, in SO_3 and SF_6 ; osmium, a Group VIII element, can have a valency of eight, as is the case in OsO_4 and OsF_8 . For a full treatment of the significance of this fact, and for a proper discussion of the periodic classification, the student is referred to textbooks of general chemistry.

By chemical means, the combining weight, or equivalent of an element may be determined; for the determination of the atomic weight, a knowledge of the valency is also required, *i.e.*, a knowledge of which multiple of the equivalent weight is to be accepted as the atomic weight. The principal methods of fixing the value of the atomic weight, given a knowledge of the equivalent, may now be considered.

CANNIZZARO'S "ABSOLUTE" METHOD

This method of fixing the true values of the atomic weights, advanced by Cannizzaro in 1858, involves as its only assumption the truth of Avogadro's hypothesis, now well established, and it may accordingly be considered an "absolute" method. Prior to 1858, Avogadro's hypothesis had remained unaccepted for nearly fifty years. Atomic weights rested upon an essentially arbitrary basis, different values being accepted by different chemists (*e.g.*, oxygen = either 8 or 16). In consequence, there were no consistent grounds for the assignment of formulæ, water, for example, being variously written HO or H_2O according to the scale of atomic weights chosen. The placing of atomic weights and chemical formulæ upon a logical and consistent footing may be largely

attributed to Cannizzaro's advocacy of Avogadro's hypothesis.

It has been shown in the previous chapter that acceptance of Avogadro's hypothesis enables the molecular weight of volatile compounds to be calculated from their vapour densities. If, now, a series of volatile compounds of some one element be considered, the percentage compositions of which are known, then the weight of the element present in one molecule of each of the series of its compounds may be found. From the atomic theory, one molecule of a compound contains one, or two, or some whole number of atoms of the element, never a fractional number. The weight of the element present in one molecule of each of the compounds represents, then, the weight of one or two or some other whole number of atoms of the element. The weight of one atom, then, is the highest common factor of the weights present in the various compounds considered.

This may be illustrated for the case of carbon. For a series of volatile carbon compounds the following data are found :—

	V.D.	Mol. Wt.	% C.	C in molecule
Carbon dioxide ...	22	44	27·3	12
Methane ...	8	16	75·0	12
Ethane ...	15	30	80·0	24 = 2 × 12
Acetone ...	29	58	62·1	36 = 3 × 12
Ethyl acetate ...	44	88	54·5	48 = 4 × 12
Pyridine ...	39·5	79	76·0	60 = 5 × 12
Benzene ...	39	78	92·3	72 = 6 × 12

i.e., every compound contains either 12 parts or some multiple of 12 parts by weight of carbon in one molecule. No compounds are known containing, say 42, or any amount not a multiple of 12 parts of carbon in the molecule. Hence 12 is to be adopted as representing the atomic weight of carbon.

It is plain that the application of this method of fixing atomic weights is limited to those elements which form a number of volatile compounds—*i.e.*, to the non-metals. For purposes of calculation, however, where the number of atoms of the element present in the molecule of one of

its volatile compounds may be assumed to be known, the atomic weight may be derived from its equivalent weight and the vapour density of one of its compounds.

Example. Antimony chloride contains 53.03% of its weight of antimony, and has a vapour density of 114. If there is but one atom of antimony in the molecule of antimony chloride, what is the atomic weight of antimony?

First find the equivalent.

46.97 gm. chlorine unite with 53.03 gm. antimony

35.46 " " " " $\frac{85.46}{46.97} \times 53.03$ gm. antimony

\therefore equivalent of antimony = 40.01

Hence the atomic weight of antimony = $40.01 \times n$.

the formula of the chloride = SbCl_n , since it contains 1 atom of antimony, n being the valency.

Since the vapour density of the chloride = 114

\therefore the molecular weight = 228

Weight of antimony in the molecule = $0.53 \times 228 = 121$

valency = $\frac{\text{approx. atomic weight}}{\text{equivalent weight}} = \frac{121}{40}$

i.e., the valency = 3

\therefore true atomic weight = $3 \times 40.01 = 120.03$.

Formula of the chloride = SbCl_3 .

THE RULE OF DULONG AND PETIT

It was found by Dulong and Petit in 1819 that for elements in the solid state, the product of the atomic weight and the specific heat was about the same for all the elements examined. This product is termed the *atomic heat*.

				Atomic Weight	Specific Heat	Atomic Heat
7	Lithium	6.94	0.9408	6.53
27	Aluminium	27.03	0.2143	5.81
56	Iron	55.84	0.1098	6.12
63.5	Copper	63.57	0.0923	5.88
108	Silver	107.9	0.0559	6.03
197	Gold	197.2	0.0304	6.25
207	Lead	207.2	0.0315	6.52
238	Uranium	238.5	0.0277	6.61

It may be seen from the table that the atomic heat is, in fact, roughly constant, even for elements differing in atomic weight as much as lithium and uranium. The

value 6.4 is usually adopted as representing a mean value for this "constant." Four elements, however, form exceptions to this rule of the constancy of the atomic heat, viz. :—

	Atomic Weight	Atomic Heat
Carbon (diamond)	12	1.35
Beryllium	9	3.4
Boron	11	2.6
Silicon	28.3	4.8

It must be realised that the specific heat of any element varies with the temperature at which it is measured, although for most elements the temperature coefficient is small. The four elements whose atomic heats are anomalous, however, are found also to show a large variation of specific heat with temperature. Thus the specific heat of boron changes from 0.191 at -40° to 0.366 at 223° ; that of carbon (in the form of diamond) changes from 0.113 at 10° to 0.462 at 1000° . The atomic heats measured at elevated temperatures tend to approach steady values, and are found to be of the same order as for the elements conforming to Dulong and Petit's rule :

<i>e.g.</i> , for carbon at 1000° ,	atomic heat = 5.55
beryllium at 500°	5.61
boron at 300°	4.5
silicon at 230°	5.68

As the temperature is raised, the anomaly shown by these four elements as compared with the majority of the elements disappears. In an exactly similar way, the specific heats of all elements begin to decrease rapidly at low temperatures, and measurements of the atomic heats of the normal elements at very low temperatures show amongst themselves divergences as great as those exhibited by carbon, beryllium, boron and silicon at room temperature.

In general, therefore,

atomic weight \times specific heat = 6.4 approximately

i.e., $\frac{6.4}{\text{specific heat}} = \text{approximate atomic weight.}$

An approximate value for the atomic weight may, there-

fore, be obtained from a knowledge of the specific heat, and that multiple of the equivalent then selected which approximates to this figure.

Example. 2.1461 gm. cobalt oxide gave on reduction 1.6868 gm. of cobalt. If the specific heat of cobalt is 0.103, what value does this experiment give for the atomic weight of cobalt?

Since 2.1461 gm. of cobalt oxide contain 1.6868 gm. of cobalt,

0.4593 gm. of oxygen combine with 1.6868 gm. of cobalt

$$\therefore 8 \text{ gm. } \quad \quad \quad \quad \quad \quad \quad \quad \frac{8.000}{0.4593} \times 1.6868 \text{ gm. of cobalt}$$

$$= 29.37 \text{ gm.}$$

$$\therefore \text{equivalent of cobalt} = 29.37$$

$$\therefore \text{atomic weight of cobalt } 29.37 \times n$$

By Dulong and Petit's rule, the approximate atomic weight is

$$\frac{6.4}{0.103} = 62$$

Since $29.37 \times n = \text{roughly } 62$, i.e., $n = 2$.

i.e., the true atomic weight = 58.74

Application of Dulong and Petit's rule actually proved of value in fixing the correct atomic weight of indium. The equivalent weight of indium was found to be 37.8. From certain similarities of its chemical properties to those of zinc, it was at first considered that indium was bivalent, giving 75.6 as the atomic weight. The specific heat of the metal was subsequently found to be 0.057, so that the atomic weight should be about 112. Indium must therefore actually be trivalent, with the atomic weight $3 \times 37.8 = 113.4$, a conclusion justified by the later study of its chemical properties.

MITSCHERLICH'S LAW OF ISOMORPHISM

The work of Haüy at the beginning of the nineteenth century established the fact that the crystalline form of any substance is characteristic of that substance, and, as was at first considered, peculiar to it. By *crystalline form* is meant, not the appearance of the crystal, since the relative development of different sets of faces may be greatly in-

fluenced by the conditions under which the crystal grows, but the *symmetry* of the crystal and the size of the *interfacial angles*. Mitscherlich observed in 1818 that different compounds—the phosphates and arsenates of potassium and ammonium—could possess the same crystalline form. Such substances he termed *isomorphous*, and from his study of the phenomenon he enunciated the law that the same number of atoms, united in the same kind of way, produce the same crystalline form; i.e., if two compounds are isomorphous, they may be represented by similar formulæ. Thus, the first isomorphous salt pairs investigated by him were KH_2PO_4 and KH_2AsO_4 ; $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{HAsO}_4$; $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and $\text{NaH}_2\text{AsO}_4 \cdot \text{H}_2\text{O}$, in each of which the sole difference between the two members is the replacement of one phosphorus atom by one arsenic atom.

Many series of isomorphous compounds are now known. Potassium alum, for example,



is a member of the group of so-called "alums," all of which may be expressed by the general formula $\text{M}_2^{\text{I}}\text{SO}_4 \cdot \text{M}_2^{\text{III}}(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, where M^{I} may be any of the metals Na, K, (NH_4) , Rb, Cs, or Tl, and where M^{III} may be Al, Cr, Mn, Fe, or Tl. The double sulphates of the type of $\text{K}_2\text{SO}_4 \cdot \text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ form another large group of isomorphous salts. Potassium may be replaced by other univalent metals, cobalt by other divalent metals, and even the sulphate radical replaced by the selenate radical. Numerous isomorphous series, illustrating Mitscherlich's law, are found amongst minerals. In each, the general type of formula is the same, the crystalline form being unaltered by substitution of one atom by another. Such isomorphous minerals are:—

Calcite CaCO_3 ,	Aragonite CaCO_3 ,	Celestine SrSO_4 ,
Dolomite $(\text{Ca}, \text{Mg})\text{CO}_3$,	Strontianite SrCO_3 ,	Barytes BaSO_4 ,
Chalybite FeCO_3 ,	Witherite BaCO_3 ,	Anglesite PbSO_4 ,
Dialogite MnCO_3 ,	Cerussite PbCO_3 ,	

Isodimorphism. As may be seen from the above table of isomorphous minerals, calcium carbonate can crystallise in two distinct forms: trigonal calcite and rhombic

aragonite. Such a substance is termed *dimorphous*. Arsenious oxide may similarly crystallise either as octahedral or as rhombic crystals, which are each isomorphous with octahedral and rhombic forms respectively of antimony trioxide. Arsenious oxide and antimony trioxide are accordingly said to be *isodimorphous*. In a similar way, stannic oxide, SnO_2 , and titanium dioxide, TiO_2 , are *isotrimorphous*.

CRITERIA OF ISOMORPHISM

Accurate measurement shows that the interfacial angles of isomorphous crystals are not rigidly identical, but differ within narrow limits for different members of a series. In the double sulphates referred to above, the value of a particular interfacial angle varies from $69^\circ 40'$ in the case of $\text{Cs}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ to $74^\circ 58'$ for $\text{K}_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ —a range of over 2° between the extremes. Isomorphous substances are therefore not identical, but only closely similar in their crystalline form. Moreover, certain cases are known where compounds are similar in crystalline form, but do not conform to Mitscherlich's law of analogous formulæ, and so cannot be considered as strictly isomorphous. Such is the case with galena, PbS and argentite Ag_2S . It is therefore necessary to seek other criteria to define isomorphism accurately; two further indications of isomorphism have been proposed.

(1) Isomorphous substances should form a complete range of *mixed crystals* or *solid solutions*, containing from 100% of one constituent to 100% of the other, and the physical properties of the crystals formed—colour, density, refractive index, etc.—should be an unbroken linear function of the composition.

(2) *Isomorphous overgrowths* should be formed when one crystal is placed in a saturated solution of the other isomorph. Thus the violet octahedral crystals of chrome alum continue to grow, and become coated with a colourless layer of potassium aluminium alum when they are placed in a saturated solution of that salt.

THE APPLICATION OF THE LAW TO THE DETERMINATION OF ATOMIC WEIGHTS

(1) The examples of isomorphous compounds cited above show that isomorphism implies atom-for-atom replacement of one element by another. If then, two isomorphous compounds be considered, one consisting of elements of known atomic weight, the other containing an element of unknown atomic weight, the latter may be compared directly with that of the element it replaces.

Example. Potassium sulphate and selenate are isomorphous, and have the compositions K 44.83%, O 36.78%, S 18.39%; and K 35.29%, O 28.96%, Se 35.75% respectively. What is the atomic weight of selenium?

First, find the weight of selenium combined with 44.83 parts by weight of potassium = $\frac{44.83}{35.29} \times 35.75$ parts
= 45.40 parts

hence, 45.40 parts of Se replace 18.39 parts of S, being combined with 44.83 parts of potassium in the two salts.

Since the compounds are isomorphous,

1 atom of Se replaces 1 atom of S

$$\therefore \frac{\text{Atomic weight of Se}}{\text{Atomic weight of S}} = \frac{\text{Atomic weight of Se}}{32.07} = \frac{45.40}{18.39}$$

$$\therefore \text{atomic weight of selenium} = \frac{45.40 \times 32.07}{18.39} = 79.1$$

(2) Comparison of the compounds of an element, the atomic weight and valency of which are known, with the isomorphous compounds of an "unknown" element indicates the valency of the latter. From a determination of the equivalent, it is then possible to deduce the atomic weight.

Example. Radium bromide is isomorphous with barium bromide, $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$. Thorpe found the equivalent of radium to be 113.3. What is its atomic weight?

Since radium bromide and barium bromide are isomorphous, radium bromide is $\text{RaBr}_2 \cdot 2\text{H}_2\text{O}$.

\therefore radium is divalent.

$$\therefore \text{atomic weight of radium} = 2 \times \text{equivalent weight} \\ = 2 \times 113.3 = 226.6.$$

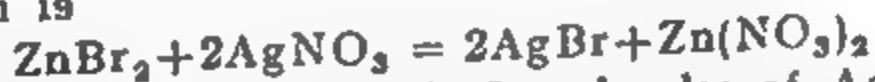
THE ACCURATE DETERMINATION OF ATOMIC WEIGHTS

It must be clearly understood that the methods discussed above, based upon vapour density determinations, Dulong and Petit's rule, and isomorphism, serve only to fix the magnitude of the atomic weight of an element. Accurate atomic weights may, indeed, be calculated in certain cases from gas density data (*e.g.*, determinations of the atomic weight of nitrogen from the density of nitrogen and of nitric oxide, cf. Rayleigh, *Proc. Roy. Soc.*, 1894, 65, 340), but in general an accurate value for the chemical equivalent must be determined gravimetrically.

Since the days of Stas, much attention has been paid to the refinement of atomic weight determinations. The direct methods of equivalent determination described in Chapter I do not, in most cases, lend themselves to sufficient accuracy for atomic weight purposes. As a result of much experience, especially of the painstaking classical researches of T. W. Richards at Harvard, it has been found that the compounds most generally suited for use in atomic weight determinations are the chlorides and bromides of the elements, which may in most cases be prepared in a state of absolute purity, and which lend themselves to accurate manipulation. The method most frequently used, accordingly, is the determination of the weight of silver halide obtainable from a known weight of the chloride or bromide in question. Then, the atomic weights of silver and of chlorine or bromine being known, the equivalent of the element may be calculated.

Example. Richards and Rogers found that 59.96 parts by weight of zinc bromide yielded 100 parts of silver bromide on treatment with silver nitrate. Calculate the atomic weight of zinc, if $\text{Ag} = 107.9$, $\text{Br} = 79.92$. Zinc is known to be bivalent.

Since zinc is bivalent, zinc bromide has the formula ZnBr_2 . The reaction is



i.e., 1 molecule of ZnBr_2 yields 2 molecules of AgBr .

$\therefore (\text{Zn} + 2 \times 79.92)$ parts of ZnBr_2 yield $2 \times (107.9 + 79.92)$ parts of AgBr .

$$\frac{\text{Weight of ZnBr}_2}{\text{Weight of AgBr}} = \frac{\text{Zn} + 159.84}{375.6} = \frac{59.96}{100.0} \quad . \quad . \quad \text{from the data.}$$

$$\therefore \text{Zn} = \frac{59.96 \times 375.6}{100} - 159.84$$

$$= 65.38.$$

The application of such a method presupposes a knowledge of the atomic weights of silver and chlorine or bromine. This, in turn, involves a very accurate knowledge of (a) the composition of silver chloride and silver bromide, and (b) the combining weight of silver relative to oxygen, since $\text{O} = 16$ is the standard relative to which atomic weights are measured.

The compositions of silver chloride and of silver bromide are known with great accuracy. Not only have direct determinations been made of the weight of silver chloride and silver bromide formed from a known weight of silver, but in atomic weight determinations by analysis of chlorides or bromides, the quantity of silver required to react is frequently determined in addition to the amount of halide formed, so that the "cross-ratio" AgBr/Ag or AgCl/Ag so obtained forms a check on the accuracy of the determination. The work of Richards and Wells (*J.A.C.S.*, 1905, 27, 517) may profitably be read as illustrative of the technique and precautions involved in the most accurate work.

Since the standard of atomic weights is the weight of the oxygen atom, while the most frequently adopted method of atomic weight determination measures atomic weights directly relative to silver, the determination of the accurate atomic weight of silver is of the highest importance. Any error attending this value will be involved in all other determinations. Two general ways are available by which the atomic weight of silver may be found. The amount of silver in salts rich in oxygen—silver nitrate or silver sulphate—may be found, and the ratios AgNO_3/Ag , $\text{Ag}_2\text{SO}_4/2\text{Ag}$ so found may be then combined with independent data for the atomic weight of the third element—*e.g.*, with the atomic weight of nitrogen as determined from gas density determinations. Such a

method inevitably involves a multiplication of errors, and a more direct method is desirable.

Stas sought to achieve this by using iodates and chlorates, but the substances proved to be unsuited to the most accurate work. Richards and Willard converted lithium chloride to lithium perchlorate, obtaining the ratio $\text{LiClO}_4 / \text{LiCl}$, i.e., $4 \text{ O} / \text{LiCl}$. A determination of the amount of silver chloride obtained from a known weight of lithium chloride then gave the ratio LiCl / Ag , which on combination with the other gives the ratio of the weight of four atoms of oxygen to the weight of one atom of silver :—

$$\frac{4 \text{ O}}{\text{LiCl}} \times \frac{\text{LiCl}}{\text{Ag}} = \frac{4 \text{ O}}{\text{Ag}}$$

The most accurate direct determination of the atomic weight of silver, relative to oxygen, is that of O. Honigsmid and R. Sachtleben (*Zeit. anorg. Chem.*, 1929, **178**, 1), which illustrates the most modern refinements of experimental work of this kind. Barium perchlorate was converted to barium chloride by heating in hydrogen chloride, and the amount of silver required to react with the barium chloride then determined. Then,

$$\frac{\text{Loss in weight of the Ba(ClO}_4)_2}{\text{Weight of silver required}} = \frac{\text{Weight of 4 atoms of oxygen}}{\text{Weight of 1 atom of silver}}$$

Thus, in their experiments, 51.83992 gm. of barium perchlorate yielded 32.10713 gm. of barium chloride (i.e., lost 19.73279 gm. of oxygen), which reacted with 33.26223 gm. of silver.

$$\frac{\text{Ag}}{4 \text{ O}} = \frac{33.26223}{19.73279} = 1.68563$$

$$\therefore \text{Ag} = 1.68563 \times 64.000 = 107.880.$$

THE INTERRELATION OF THE ATOMIC WEIGHTS

The determinations discussed in the last section are actually determinations of equivalents. The accepted atomic weights of the elements, and the formulæ of their compounds have been fixed by the application of the

methods outlined in this chapter. Cannizzaro's absolute method forms the ultimate basis of the values assigned to the non-metals, which form volatile compounds—H, B, C, N, O, F, P, S, Cl, Br. The other elements are linked up with these (a) by considerations of isomorphism. Thus K_2SO_4 , K_2SeO_4 , and K_2CrO_4 are isomorphous, as are also $KClO_4$ and $KMnO_4$. Thus the true atomic weights of Se, Cr, Mn may be fixed. But Mn, Fe, Co, Ni, Cu, Zn, Cd form isomorphous sulphates, as also do Cr, Fe, Al, Ti. Thus these elements in turn have their valency established. Extension of such reasoning includes almost all the elements.

(b) The values obtained by the application of the law of isomorphism serve to confirm the approximate validity of the rule of Dulong and Petit, which may then be employed to fix the magnitude of the atomic weight of any elements not established beyond doubt by considerations of isomorphism.

PROBLEMS ON ATOMIC WEIGHT DETERMINATIONS

(The answers to problems with odd numbers will be found at the end of the book)

The following atomic weights may be assumed where necessary

$$\begin{array}{lll} Ag = 107.88 & Cl = 35.46 & Br = 79.92 \\ N = 14.00 & S = 32.07 & \end{array}$$

- 206 2.327 gm. of a metal yielded 8.578 gm. of its bromide. Calculate the equivalent of the metal, and its atomic weight if the specific heat = 0.055.
- 207 0.4257 gm. of the chloride of a metal leave on strong ignition a residue of the metal weighing 0.2760 gm. The specific heat of the metal = 0.0328. What is its atomic weight?
- 208 A sample of a metallic oxide containing 2.7 gm. of the metal, gave up all its oxygen on heating, the volume liberated being 140 c.c. at N.T.P. Find the equivalent of the metal, and its atomic weight if the specific heat is 0.058.
- 209 On dissolving 0.444 gm. of a metal, of specific heat 0.107, in acid, 177 c.c. of hydrogen were liberated, measured dry at 10° and 750 mm. Find the atomic weight of the metal.

- 210 1.62 gm. of a metal were heated in a current of oxygen. 3.06 gm. of oxide were obtained. Calculate the equivalent of the metal, and its atomic weight if the specific heat is 0.218.
- 211 1.334 gm. of lithium chloride gave on evaporation with nitric acid 2.169 gm. of lithium nitrate. The specific heat of lithium is 0.941. Calculate its atomic weight, assuming that $\text{Cl} = 35.46$, $\text{N} = 14.00$ when $\text{O} = 16$.
- 212 1.9166 gm. of copper oxide gave on reduction 1.5298 gm. of copper. If the specific heat of copper = 0.0923, find its atomic weight.
- 213 3.7707 gm. of bismuth bromide, when dissolved in water and treated with silver nitrate, yielded 4.7432 gm. of silver bromide. The specific heat of bismuth is 0.0305. What is its atomic weight, and what is the formula of its bromide?
- 214 3.6263 gm. of silver, dissolved in nitric acid to form silver nitrate, were required to precipitate completely the chlorine in 4.6724 gm. of lead chloride. Find the atomic weight of lead, if the specific heat = 0.0315.
- 215 Baxter found that 3.559 gm. of ferrous bromide gave 6.199 gm. of silver bromide on treatment with silver nitrate. Calculate the atomic weight of iron, given that its specific heat is 0.1098.
- 216 The specific heat of uranium is 0.0277. 1.800 gm. of uranium bromide required 1.392 gm. of silver for precipitation. Calculate the atomic weight of uranium.
- 217 3.5834 gm. of potassium platichloride gave on heating in hydrogen 1.1001 gm. of potassium chloride and 1.4372 gm. of platinum. The specific heat of platinum is 0.0324. What is its atomic weight?
- 218 1.7210 gm. of samarium sulphate (anhydrous) yielded on ignition 1.0195 gm. of the corresponding oxide. The specific heat of samarium is about 0.04. Determine its atomic weight.
- 219 31.7 gm. of zinc were dissolved in sulphuric acid, and the hydrogen evolved was burned to form water. 8.671 gm. of water were obtained. If the specific heat of zinc is 0.094, what value does this experiment give for the atomic weight?
- 220 Marignac found that 1.8680 gm. of magnesium oxide were converted by heating with sulphuric acid to 5.5715 gm. of anhydrous magnesium sulphate. The specific heat of magnesium is 0.25. Find the atomic weight of magnesium.
- 221 Sodium hydrogen arsenate is isomorphous with sodium hydrogen phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$. Analysis shows that it contains 18.64% of arsenic. Calculate the atomic weight of arsenic.

- 222 Sodium metaphosphate, NaPO_3 , and sodium metavanadate are isomorphous. 4.856 gm. of sodium metavanadate, when heated in a stream of chlorine+hydrogen chloride, left a residue of 2.328 gm. of sodium chloride. Find the atomic weight of vanadium.
- 223 Potassium chromate and potassium sulphate are isomorphous. 6.567 gm. of silver chromate, when treated with hydrochloric acid, yielded 5.674 gm. of silver chloride. It is known that silver chromate contains no water of crystallisation. What is the atomic weight of chromium?
- 224 Thallous sulphate forms with cobalt sulphate a double salt isomorphous with ferrous ammonium sulphate, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. If thallous sulphate contains 80.95% of thallium, what is the atomic weight of thallium?
- 225 The salts of caesium are isomorphous with the corresponding potassium salts. 3.3333 gm. of caesium nitrate were heated with pure silica, thereby expelling N_2O_5 . The loss in weight amounted to 0.9242 gm. What is the atomic weight of caesium?
- 226 Cadmium sulphate and zinc sulphate are isomorphous. 6.754 gm. of anhydrous cadmium bromide were treated with silver nitrate. 9.318 gm. of silver bromide were obtained. Find the atomic weight of cadmium.
- 227 Naturally occurring strontium sulphate, celestine, is isomorphous with anhydrite, anhydrous calcium sulphate. Thorpe and Francis found that 5.305 gm. of strontium sulphate could be obtained from 7.146 gm. of anhydrous strontium bromide. Calculate the atomic weight of strontium.
- 228 Gallium sulphate and ammonium sulphate form a double salt isomorphous with ordinary alum. 3.1044 gm. of this salt left on ignition 0.5885 gm. of gallium oxide. Deduce from these data the atomic weight of gallium.
- 229 Native titanium oxide, rutile, is isomorphous with native stannic oxide, cassiterite. By the decomposition of 6.589 gm. of titanium chloride with water, and ignition of the product, 2.770 gm. of titanium oxide were obtained. Calculate the atomic weight of titanium.
- 230 Potassium perrhenate is isomorphous with potassium permanganate. If silver perrhenate contains 30.12% of silver, calculate the atomic weight of rhenium.
- 231 When 1.599 gm. of silver selenite were heated in hydrogen chloride, 1.336 gm. of silver chloride were obtained. Find the atomic weight of selenium, knowing that potassium selenite is isomorphous with potassium sulphite.

- 232 Potassium manganate, a compound isomorphous with potassium sulphate, contains 27.86% of manganese. Find the atomic weight of manganese.
- 233 Potassium perruthenate is isomorphous with potassium perchlorate. It contains 50.15% of ruthenium. What is the atomic weight of ruthenium?
- 234 Rubidium salts and potassium salts are isomorphous. 2.000 gm. of rubidium chloride gave 2.371 gm. of silver chloride when the solution was treated with silver nitrate. Calculate the equivalent weight and atomic weight of rubidium.
- 235 Anglesite, native lead sulphate, and barytes, native barium sulphate BaSO_4 , are isomorphous. Stas found that pure lead sulphate contained 68.29% of lead. Calculate the atomic weight of lead.
- 236 A metallic chloride contains 45.6% of the metal, and its vapour density is 130. If the molecule of the chloride contains only one atom of the metal, find its atomic weight and the formula of the chloride.
- 237 Baker and Bennett found that tellurium bromide contained 28.52% of tellurium. Its vapour density is 223. Find the atomic weight of tellurium, stating any assumptions involved.
- 238 1.771 gm. of zirconium chloride, of vapour density 116, were hydrolysed by water and treated with silver nitrate, 4.349 gm. of silver chloride were obtained. Find the equivalent weight and the atomic weight of zirconium, assuming the presence of one atom of metal in the molecule of the chloride.
- 239 By reduction of 10.433 gm. of tungsten chloride, 4.837 gm. of tungsten were obtained. The vapour density of the chloride was found to be nearly 200, and the molecule is known to contain only one atom of tungsten. Find the formula of the chloride and the atomic weight of the metal.
- 240 It was found that 355 c.c. of boron chloride vapour weighed 1.679 gm. at 25° and 750 mm. 8.089 gm. of the compound required 22.88 gm. of silver for complete precipitation. Calculate the atomic weight and the equivalent weight of boron.
- 241 0.836 gm. of titanium chloride, vaporised in a Victor Meyer apparatus, displaced 103.1 c.c. dry air at 17° and 771 mm. pressure. 4.201 gm. of the chloride, treated with water and silver nitrate, gave 12.68 gm. of silver chloride. Find the atomic weight of titanium.
- 242 The weight of 1 litre of arsenic hydride at 0° and 760 mm. is 3.480 gm. 7.660 gm. of arsenic chloride reacted with the silver nitrate derived from 13.686 gm. of silver. Find the atomic weight of arsenic.

- 243 1 gm. of an element gave on calcination 1.32 gm. of solid oxide. 100 c.c. of the gaseous hydride, collected over mercury in a tube closed by a porous plug and exposed to the air, changed in volume until a final steady volume of 164 c.c. was attained. What is the molecular weight of the hydride, and the atomic weight of the metal, if the molecule of the hydride contains one atom of the metal?
- 244 By the hydrolysis of 7.164 gm. of silicon chloride and ignition of the product, 2.536 gm. of silicon oxide were obtained. The simplest hydride of silicon has a rate of diffusion 1.165 times that of carbon dioxide. Determine the atomic weight of silicon.
- 245 Winkler found that germanium chloride contained 66.17% of chlorine. 60.5 c.c. germanium hydride diffuse through an aperture in the same time as 100 c.c. of nitrogen (under similar conditions of temperature and pressure). The molecule of the hydride contains one atom of germanium. Calculate the atomic weight of germanium.

CHAPTER V

ELECTROLYSIS AND THE IONIC THEORY: MOLECULAR WEIGHT OF DISSOLVED SUBSTANCES

ELECTROLYSIS

The solutions in water of acids, bases and salts, possess the property of conducting electricity, a property not possessed by pure water, by solutions of neutral substances (*e.g.*, cane sugar) or even by substances such as liquid hydrogen chloride.

The conduction of electricity through solutions differs, however, from conduction through metals in that the passage of the current is attended by the decomposition of the dissolved substance. If an electric current be passed through a solution of copper sulphate, copper is deposited upon the electrode connected to the negative terminal of the battery, at which the current leaves the solution (the *cathode*), while oxygen is evolved at the positive electrode (the *anode*). If the anode is made of copper, instead of oxygen being given off, copper is dissolved from the material of the electrode. The operation is known as *electrolysis*, and substances whose solutions conduct electricity are termed *electrolytes*. Solutions of salts in certain solvents other than water, and fused salts are also electrolytes. It is found that the metallic constituent of a salt, or hydrogen in the case of an acid, is always liberated at the cathode; the acidic constituent is correspondingly liberated at the anode, although the actual products isolated may result from the reaction of the direct products of electrolysis with water. Thus electrolysis of sodium hydroxide solution yields hydrogen

and oxygen as actual products, both of which are really the result of secondary reactions with the water (see below, p. 93). The oxygen liberated at the anode in the electrolysis of copper sulphate arises similarly, and is accompanied by the formation of sulphuric acid around the electrode.

FARADAY'S LAWS OF ELECTROLYSIS

Investigation of the phenomena of electrolysis by Faraday led to the discovery of two laws relating the amount of chemical action effected to the quantity of electricity passed through the solution.

For the same electrolyte, the amount of chemical action—i.e., the amount of the products liberated at the electrodes—is directly proportional to the quantity of electricity passed, and is independent of the temperature, the strength of the current, the concentration of the solution, or any other variable factor. The passage of one coulomb (amount of electricity in coulombs = current in amperes \times time of flow in seconds) through a solution of silver nitrate causes the deposition of 0.0011183 gm. of silver at the cathode: the passage of 20 coulombs therefore deposits $20 \times 0.0011183 = 0.022366$ gm., of 2,000 coulombs 2.2366 gm. of silver, etc.

This direct proportionality between electrolytic action and quantity of electricity passed is applied to the accurate measurement of electricity by determination, for example, of the weight of silver deposited on the cathode of a *silver voltameter*, or sometimes of iodine liberated at the anode of an iodine voltameter. On a large scale, the method is employed in "electrolysis meters," where the volume of mercury deposited, at a constant, known supply voltage, forms a measure of the power consumption. The liberation of other substances—copper, hydrogen, etc., may also be employed, but the iodine and silver voltameters are susceptible of the most accurate results.

Example. An electric current was passed for 25 minutes through a silver voltameter. It was found that 0.1795 gm. of silver were deposited. What was the mean value of the current?

First, find the quantity of electricity passed.

1 coulomb deposits 0.001118 gm. of silver

\therefore 0.1795 gm. is deposited by $\frac{0.1795}{0.001118}$ coulombs = 160.5 coulombs

Hence, 160.5 coulombs pass in 25×60 seconds

i.e., mean current = $\frac{160.5}{25 \times 60}$ ampères = 0.107 amp.

The relation between the quantities of different substances deposited by the same amount of electricity is given by Faraday's second law. If a number of cells containing different electrolytes are connected in series, so that the same current flows through each, the amounts of the different products liberated by electrolysis are found to be proportional to their chemical equivalents. If the current is passed through solutions of silver nitrate, copper sulphate, dilute sulphuric acid, gold chloride, and potassium iodide, 0.1079 gm. of silver (0.001 gram equivalents) being deposited in the silver voltameter, it is found that in the other cells, 0.0318 gm. of copper, 0.00101 gm. of hydrogen, 0.0080 gm. of oxygen, 0.0657 gm. of gold and 0.1269 gm. of iodine are liberated, i.e., 0.001 gram-equivalents in each case.

It has already been stated that 1 coulomb deposits 0.0011183 gm. of silver. 1 gram-equivalent would there-

fore be deposited by $\frac{107.88}{0.0011183}$ coulombs, = 96,500

coulombs. This quantity is termed one faraday. The amount of any substance liberated by the passage of 1 coulomb is known as the *electrochemical equivalent*. Faraday's second law may be re-stated: the electrochemical equivalent of any substance is proportional to its chemical equivalent. One gram equivalent of a substance is liberated by the passage of one faraday.

Example 1. 500 coulombs of electricity are passed through a solution of stannic chloride, SnCl_4 . What weight of tin is deposited on the cathode?

The chemical equivalent of tin = $\frac{118.7}{4} = 29.7$

i.e., 96,500 coulombs deposit 29.7 gm. of tin

\therefore 500 " " $\frac{29.7 \times 500}{96,500}$ gm. = 0.1508 gm.

Example 2. 0.1978 gm. of copper were deposited by a current of 0.2 amps. in 50 minutes. What is the electrochemical equivalent of copper?

$$\begin{aligned}\text{Quantity of electricity passed} &= 0.2 \times 50 \times 60 \text{ coulombs} \\ &= 600 \text{ coulombs}\end{aligned}$$

Hence 600 coulombs deposit 0.1978 gm. of copper

$$\therefore 1 \text{ coulomb deposits } \frac{0.1978}{600} \text{ gm.} = 0.0003296 \text{ gm. of copper.}$$

THE IONIC HYPOTHESIS

The facts of electrolytic conduction and of electrolysis are explained by supposing that when an electrolyte is dissolved in water it dissociates to some extent into particles, termed *ions*, bearing equal and opposite charges of electricity. On the application of an electromotive force, the ions move through the solution towards the electrodes, the positively charged ions moving to the cathode, the negatively charged ions towards the anode. The ions thus serve as the carriers of the current through the solution, and on reaching the electrodes they are discharged, and are set free as neutral chemical entities. Since the metallic radical of an electrolyte is always liberated at the cathode, it follows that the metallic ions and hydrogen ion bear a positive charge, the acid radical ions being negatively charged. In a solution of silver nitrate, therefore, a portion of the salt is dissociated into positively charged Ag^+ ions and negatively charged NO_3^- ions:—



On electrolysis, the Ag^+ ions (called *cations* since they move to the cathode) move towards and are discharged at the cathode, silver being deposited. An equivalent quantity of NO_3^- *anions* is similarly discharged at the anode. The neutral NO_3 radical is, however, incapable of an independent existence, and so does not appear as such, but reacts with water:—



Oxygen is therefore liberated at the anode as a secondary product of electrolysis. If, however the material of the anode is readily attacked by the nascent

acid radical—*e.g.*, a silver anode—reaction occurs between them: $\text{NO}_3 + \text{Ag} = \text{AgNO}_3$, silver nitrate being continuously re-formed in the solution.

Taking the positive or negative charge borne by a univalent ion such as Ag' or NO_3' as a unit, it is plain that since two NO_3 groups unite with one atom of copper to form the neutral molecule of copper nitrate $\text{Cu}(\text{NO}_3)_2$, the copper ion formed on dissociation must be doubly charged. In general, the number of unit charges borne by an ion is the same as the ordinary valency of the radical giving rise to it. The chemical properties of solutions of electrolytes are governed by the ions they contain: their reactions are reactions between ions. The similarity in properties between acids is due to the fact that all acids yield the hydrogen ion as their positive ion on dissociation. Bases similarly have the negative OH' ion in common.

Experiment shows that electrolysis commences immediately a potential difference is applied. No time appears to be required to bring about dissociation on the application of an electric field. Further, Ohm's law holds exactly for electrolytes, so that no work is expended on pulling apart the components of the molecules. On these and other grounds it is held that electrolytes are already dissociated in solution to a large degree, and that dissociation is not first brought about by the passage of the electric current. This view is supported by molecular weight determinations on solutions of electrolytes (see below), which indicate that in a solution of *e.g.*, sodium chloride, nearly twice as many particles are present as would be present if the solution contained only undissociated molecules of NaCl .

PROBLEMS ON ELECTROLYSIS

(The answers to problems with odd numbers will be found at the end of the book)

- 246 Cells containing solutions of mercurous nitrate and cadmium sulphate respectively are connected in series with a silver voltameter. What weight of mercury and cadmium would be deposited by a quantity of electricity sufficient to deposit 0.375 gm. of silver?

- 247 1.260 gm. of copper are deposited on the cathode of a copper voltameter. What weight of iodine would be liberated at the anode of a cell filled with potassium iodide connected in series? If the anode of the latter were made of zinc, what weight of zinc would be dissolved?
- 248 What weight of gold would be deposited by the electrolysis of auric chloride solution (AuCl_3), when 2.5 litres of hydrogen (measured dry at N.T.P.) were liberated at the cathode of a cell, filled with dilute caustic soda, placed in series?
- 249 What weight of silver would be deposited per hour by the passage of a current of 0.12 ampère through a solution of silver nitrate?
- 250 What volume of electrolytic gas, collected over water at 17° and 755 mm., would be generated in the course of 3 hours by a current of 0.353 amp.?
- 251 A current of 0.250 amp. is passed for 45 mins. through an acid solution of cuprous chloride. What weight of copper is deposited on the cathode? If a copper anode is used, what is its loss in weight?
- 252 What quantity of electricity is required for the deposition of 3.088 gm. of tin from a solution of stannic chloride?
- 253 In the course of 12 hrs. electrolysis, 4.8 gm. of silver were deposited on the cathode of a silver voltameter. Calculate the mean value of the current.
- 254 0.635 gm. of iodine was liberated at the anode of an iodine voltameter during 2 hrs. 40 mins. Calculate the mean current during that period.
- 255 1.186 gm. of copper were deposited by the electrolysis of a solution of copper sulphate by a current of 0.25 amp. in 4 hrs. Calculate the electrochemical equivalent of copper.
- 256 A silver voltameter was connected in series with a cell containing an acid solution of antimony chloride. 0.880 gm. of antimony were deposited at the cathode of the latter, and 2.370 gm. of silver in the former. Find the electrochemical equivalent of antimony. The electrochemical equivalent of silver is 0.001118 gm. coulomb.
- 257 0.1744 gm. of platinum were deposited in 50 mins. by a current of 0.115 amp. Find the electrochemical equivalent of platinum.

THE CONDUCTIVITY OF ELECTROLYTES

For a description of the experimental methods involved in the determination of the conductivity of electrolytes, the student is referred to text-books of general chemistry.

The resistance of a solution between platinum electrodes a sq. cm. in area, l cm. apart is measured. The observed

resistance $R = r \times \frac{l}{a} = \frac{1}{\kappa} \times \frac{l}{a}$, where r = the specific resist-

ance of the solution, or $\kappa = \frac{1}{r}$ = the specific conductivity,

i.e., the conductivity of the solution between the faces of a cell 1 sq. cm. in area, 1 cm. apart. The quantity l/a is called the *cell-constant*, and may be found for any particular cell by determining its resistance when filled with a solution of accurately known specific conductivity—e.g., $N/50$ KCl (see footnote p. 97).

The conductivity of a solution is decreased when the solution is diluted, since fewer ions are present in unit volume to carry the current. If no new ions were produced by dilution, the conductivity should vary inversely as the concentration. It is found, however, that the conductivity does not decrease as rapidly as concentration. Accordingly, it is of importance to know the value of the

ratio $\frac{\text{Conductivity}}{\text{Concentration}}$ for different concentrations. This

may be expressed κV , where V is the *dilution* ($= 1/\text{concentration}$) i.e., the volume of solution, containing either one gram equivalent or one gram molecule of solute. In the former case, expressing V in c.c., $\Lambda_v = V_v \times \kappa$ is the *equivalent conductivity* of the solution. This would be the conductivity of that volume of solution containing one gram equivalent of electrolyte if placed between parallel electrodes 1 cm. apart, so that all the ions produced by the dissociation of one gram equivalent (at that concentration) were operative in carrying the current. Similarly, the *molecular conductivity* $\mu_o = \kappa \times V_m$, where V_m is the volume of solution in cubic centimetres, containing one gram molecule of dissolved substance. For electrolytes of the type of KCl, the equivalent weight and molecular weight of which are the same, Λ_v and μ_o are identical. In the case of electrolytes such as H_2SO_4 or $CaCl_2$, the

equivalent weights are half the molecular weights,* so that in this case $\mu_v = 2 \times \Lambda_v$.

It is found that Λ (or μ) increases with dilution, indicating that as the solution becomes more dilute, ionisation takes place to an increasingly greater extent. The increase does not proceed indefinitely, but the values of Λ_v approach asymptotically a definite value for each electrolyte (Λ_∞ , the equivalent conductivity at infinite dilution), as is shown for KCl in the table.

Concentration gm. equiv. per litre	Dilution	Λ
1.0	1	98.27
0.2	5	107.96
0.02	50	119.96
0.005	200	124.41
0.001	1000	127.34
0.0005	2000	128.11
0.0002	5000	128.77
0.0001	10000	129.07

If the above values are plotted, they are seen to approach asymptotically a value of about $130.11 = \Lambda_\infty$. This limiting value, Λ_∞ , may be taken as the equivalent conductivity of a solution in which the electrolyte is completely ionised. For any finite dilution V , the ratio $\frac{\Lambda_v}{\Lambda_\infty} = \alpha$ is a measure of the *degree of dissociation* at that dilution.

Example. What is the degree of dissociation of potassium chloride in $N/50$ solution?

From the above table, the equivalent conductivity of a 0.02N solution = 119.96.

$$\therefore \alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{119.96}{130.11} = 92.2\%$$

* Cf. the chapter on volumetric analysis (p. 110) for a consideration of the equivalent weights of compounds. A solution containing 1 gram equivalent in 1 litre is termed a *normal* (N) solution; a solution containing 1 gram equivalent in 50 litres is termed a *fiftieth-normal* ($N/50$) solution, etc.

It is of importance to note that the value found for the degree of ionisation found in this way agrees with that calculated from other data. It will be seen in the next section that the osmotic pressure, the elevation of the boiling point and the depression of the freezing point of a solution depend on the number of molecules of the solute present. If, in a solution, the proportion α of the dissolved salt is dissociated, each molecule giving rise to n ions, there are now present for each gram-molecule of salt, $1 - \alpha$ gm. mols. of undissociated salt and $n\alpha$ gram ions, $= 1 + (n - 1)\alpha = i$ gram molecules instead of one. The value of i found from electrical conductivity measurements agrees with that found from molecular weight determinations, *e.g.*, for 0.14N KCl,

i from osmotic pressure = 1.81.

i from conductivity data = 1.86.

It may be said that all salts, the strong acids (*e.g.*, HCl, HNO₃) and the strong bases (*e.g.*, NaOH) are very highly dissociated in solution. The so-called weak acids and bases, such as acetic acid and ammonia respectively, are but little dissociated.

An alternative view, which has become increasingly popular among chemists in recent years, is that a salt in solution is completely ionised at all concentrations, but that the freedom of the ions to travel through the solution increases with dilution, becoming complete at infinite dilution. Since we know that in the crystalline state salts are completely ionised, it is probable that the same is true in strong solutions. Moreover, many facts not in accord with Arrhenius' theory may be quantitatively accounted for. The simple theory, while not strictly true, affords a convenient means of making calculations concerning many properties of dilute solutions.

PROBLEMS ON THE CONDUCTIVITY OF ELECTROLYTES

(The answers to problems with odd numbers will be found at the end of the book)

- 258 The resistance of a conductivity cell with electrodes 1.64 sq. cm. in area, 0.85 cm. apart is 5.03 ohms when the cell is filled with a normal solution of potassium bromide. Calculate the specific and molecular conductivities of potassium bromide at that dilution.
- 259 A conductivity cell has electrodes 2.00 sq. cm. in area, 1 cm. apart. Filled with 5% potassium chloride, it has a resistance of 7.25 ohms. Calculate the equivalent conductivity of the potassium chloride.
- 260 The resistance of a conductivity cell filled with 0.01 *N* silver nitrate is 901 ohms. The electrodes are 1.2 cm. in diameter, 1.1 cm. apart. Calculate the equivalent and the molecular conductivity of 0.01 *N* silver nitrate.
- 261 The resistance of a conductivity cell filled with *N*/50 KCl at 18° is 17.6 ohms. Filled with *N*/10 acetic acid the resistance is 91.8 ohms. If the specific conductivity of *N*/50 KCl at 18° is 2.399×10^{-3} mhos, find the equivalent conductivity of *N*/10 acetic acid.
- 262 A conductivity cell containing *N*/100 copper sulphate (1 molecule $\text{CuSO}_4 = 2$ equivalents) had a resistance of 754 ohms at 18°. The equivalent conductivity of *N*/50 potassium chloride is 119.9 at 18°, and the resistance of the cell filled with *N*/50 KCl is 225.1 ohms. What are the equivalent and the molecular conductivities of 0.01 *N* copper sulphate?
- 263 The specific conductivity of *N*/100 KCl at 18° is 1.224×10^{-3} ohms. A cell filled with *N*/100 KCl has a resistance of 152 ohms. Filled with *N*/1000 CaCl_2 , the resistance is 1640 ohms. Find the equivalent conductivity of *N*/1000 calcium chloride.
- 264 The specific conductivity of sodium chloride at 18° varies with concentration as follows:—
- | | | | |
|--|------------------------|------------------------|------------------------|
| Conductivity | 74.4×10^{-3} | 9.25×10^{-3} | 1.028×10^{-3} |
| Concentration (in gm. mols. per litre) | 1.0 | 0.1 | 0.01 |
| Conductivity | 1.078×10^{-4} | 1.097×10^{-5} | |
| Concentration | 0.001 | 0.0001 | |
- Show by a curve the variation with concentration of (a) specific conductivity, (b) equivalent conductivity, (c) degree of ionisation, if Λ_{∞} 111.0.

- 265 The conductivity of dichloroacetic acid at 25° varies with dilution in litres as shown:—

Conductivity $\times 10^3$	57.4	37.9	23.8	14.48	8.54	4.84	2.65	1.40
Dilution	2	4	8	16	32	64	128	256

- Λ_{∞} 385. Calculate the degree of ionisation at each of the above dilutions, and plot graphically the variation of α and Λ_v .
- 266 What is the value of an electrolytic resistance, with electrodes 18 mm. in diameter, 65 cm. apart, filled with a 1% solution of sodium chloride, for which $\Lambda = 99$?

OSMOTIC PRESSURE

If vessels containing two different gases are placed in communication with one another, diffusion occurs until the gases are uniformly mixed. The same process takes place in solutions. If a layer of water is superimposed on a strong solution of copper sulphate, diffusion proceeds until the whole is uniformly coloured, *i.e.*, perfectly homogeneous. Certain membranes—animal membranes, membranes of copper ferrocyanide deposited in the pores of unglazed earthenware, etc.—are freely permeable to water, but do not permit the passage of dissolved substances. If now a solution of some substance be separated from the solvent by such a semi-permeable membrane, the solvent alone diffuses through, tending to produce uniformity of composition on both sides by diluting the solution indefinitely. If the indefinite dilution of the solution is hindered—by the action of gravity, or by enclosing the solution, the pressure on the solution side of the membrane rises, until at a definite limiting value equilibrium is established. The phenomenon is known as *osmosis*, the pressure developed is the *osmotic pressure* of the solution.

It was found by Pfeffer that the osmotic pressure of solutions varied directly with the concentration of the dissolved substance (*i.e.*, inversely with the dilution), and was directly proportional to the absolute temperature. If V is the volume of solution containing one gram molecule of solute ($= \frac{1}{c}$) then it follows that the osmotic

pressure of a solution is connected with the dilution and the absolute temperature by the expression

$$\frac{P V}{T} = K$$

This bears a formal analogy to the gas law, and it is further found that the constant K has approximately the same value for all solvents and all dissolved substances, this value being nearly the same as the gas constant R .

Example. Pfeffer found that a 1% solution of cane sugar (molecular weight 342) had at 0° osmotic pressure of 49.3 cm. of mercury. Determine the value of K .

Here V , the volume containing 1 gram molecule = 34200 c.c.

P , the osmotic pressure = 49.3×13.6 gm./sq. cm.

$T = 273^\circ$.

$$\text{Hence } K = \frac{PV}{T} = \frac{49.3 \times 13.6 \times 34,200}{273} = 83,900 \text{ gm. cm. units.}$$

This is nearly the same as the gas constant, R , 84,760 units.

Hence it may be said that the osmotic pressure exerted by any substance in solution is the same as it would exert if it were present as a gas in the same volume as that occupied by the solution, and at the same temperature.

Solutions having the same osmotic pressure are termed *isotonic solutions*. It follows from the above that isotonic solutions are equimolecular, i.e., contain in the same volume quantities of different substances in the ratio of their molecular weights.

DETERMINATION OF MOLECULAR WEIGHTS FROM OSMOTIC PRESSURE

1 gram molecule of a gas occupies at 0°C . and 76 cm. pressure a volume of 22.4 litres. Applying the relation considered above, one gram molecule of any substance, dissolved in 22.4 litres of solution would exert at 0° an osmotic pressure of 76 cm. Hence, knowing the concentration of a solution by weight, and its osmotic pressure, the molecular weight of the solute may be calculated.

Example. A 1% solution of glycerol has an osmotic pressure of 2.65 atmospheres at 15°. What is the molecular weight of glycerol?

1000 c.c. of solution contain 10 gm. glycerol

i.e., 10 gm. glycerol, at 15° and under 2.65 atmos. occupy 1000 c.c.

i.e., 10 gm. glycerol at 0° and 1 atmo. occupy $\frac{273}{288} \times 2.65 \times 1000$

c.c.

= 2510 c.c.

But 1 gm. mol. at 0° and 1 atmo. occupies 22,400 c.c.

Weight of glycerol in 22,400 c.c. = $\frac{22,400}{2510} \times 10$ gm.

= 1 gram molecule.

∴ molecular weight = 89.

MOLECULAR WEIGHTS FROM ISOTONIC SOLUTIONS

Molecular weights may also be found by preparing isotonic solutions, one of the substance in question, and one of a substance of known molecular weight. Certain natural cells—plant cells and blood corpuscles—the walls of which are semi-permeable membranes, shrink when placed in solutions of higher osmotic pressure, and swell in solutions of lower osmotic pressure. Such cells have been utilised, notably by De Vries and Hamberger, for the investigation of isotonic solutions. Solutions in which the cells neither shrink nor swell, i.e., solutions which are really isotonic with the cell contents, are isotonic with one another.

Example. A solution of urea containing 3.55 gm. per litre is isotonic with a 2% cane sugar solution. Find the molecular weight of urea.

Since the solutions are isotonic, their molecular concentrations are the same.

A 2% cane sugar solution contains 20 gm. per litre

= $\frac{20}{342}$ gm. molecules.

∴ the urea solution contains $\frac{20}{342}$ gm. molecules per litre.

i.e., $\frac{20}{342}$ gm. mols. of urea weigh 3.55 gm.

∴ molecular weight = $\frac{20}{342} \times 3.55 = 60.8$

(molecular weight from formula 60)

In the case of electrolytes, the osmotic pressure is i times that calculated for the undissociated molecule, where i has the meaning given above (p. 98).

It should be remarked that osmotic pressure measurements are rarely sufficiently accurate for the practical determination of molecular weights.

PROBLEMS ON OSMOTIC PRESSURE

(The answers to problems with odd numbers will be found at the end of the book)

- 267 What would be the osmotic pressure at 15°C . of a 1% solution of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$)?
- 268 A 1% solution of potassium chloride is dissociated to the extent of 82%. What would be its osmotic pressure at 18° ?
- 269 A solution of glycol containing 1.82 gm. per litre has an osmotic pressure of 51.8 cm. at 10° . What is the molecular weight of glycol?
- 270 Find the molecular weight of a compound, a 1% solution of which has an osmotic pressure of 118 cms. at 12°C .
- 271 If a solution of mercuric cyanide containing 1.5 gm. per litre has an osmotic pressure of 116 mm. at 25° , what is the apparent molecular weight and the degree of dissociation of mercuric cyanide?
- 272 What would be the concentration of a solution of sucrose isotonic with a solution of urea (CON_2H_4) containing 2.5 gm. per litre?
- 273 A solution containing 1.57 gm. of lithium chloride per litre is isotonic with a solution containing 12.2 gm. of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) per litre. Calculate the degree of dissociation of the lithium chloride.
- 274 Solutions containing 20 gm. of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) per litre and 1.63 gm. of boric acid in 450 c.c. respectively are isotonic. Find the molecular weight of boric acid.
- 275 Find the molecular weight of a certain sugar, a solution of which containing 3.5 gm. per litre is isotonic with a solution of urea (CON_2H_4) containing 0.5 gm. in 357 c.c.

DETERMINATION OF MOLECULAR WEIGHT FROM THE DEPRESSION OF THE FREEZING POINT

The freezing point of solutions is lower than that of the corresponding pure solvent. Raoult (1887) discovered that for any one solvent,

(a) the depression of the freezing point by a particular dissolved substance was proportional to the concentration of the solute.

(b) solutions of different substances of the same molecular concentration had the same freezing point, e.g., solutions of 3.42 gm. of sucrose or of 0.60 gm. of urea in 100 gm. of water both have their freezing point depressed by 0.185° ; the molecular weights being 342 and 60 respectively.

The depression of the freezing point which would be brought about by dissolving one gram molecule of substance in 100 gm. of solvent is termed the *molecular depression constant* per 100 gm. of solvent.

Molecular depression constants. (per 100 gm. of solvent)	{	Water 18.5° Benzene 51.2° Acetic acid 38.5°
---	---	--

Consider the case in which w gm. of a substance of molecular weight M are dissolved in 100 gm. of solvent. The depression constant for the solvent is K , and the observed depression is f° .

M gm. of solute in 100 gm. would give a depression of K° .

Hence w gm. in 100 gm. would give a depression of

$$\frac{w}{M} \times K^\circ = f^\circ, \text{ the observed depression.}$$

$$\text{i.e., } M = \frac{w}{f} \times K$$

Example. It was found that the solution of 0.2735 gm. of hydrogen peroxide in 19.86 gm. of water lowered the freezing point 0.746° . Calculate the molecular weight of hydrogen peroxide.

100 gm. of water contain $\frac{100}{19.86} \times 0.2735$ gm. hydrogen peroxide

i.e., $\frac{100}{19.86} \times 0.2735$ gm. of hydrogen peroxide in 100 gm.

of water cause 0.746° depression

$\therefore \frac{100}{19.86} \times 0.2735 \times \frac{18.5}{0.746}$ gm. hydrogen peroxide would cause a depression of 18.5°

$$\text{Molecular weight} = \frac{100}{19.86} \times 0.2735 \times \frac{18.5}{0.746} = 34.2$$

DETERMINATION OF DEGREE OF DISSOCIATION OR ASSOCIATION FROM THE DEPRESSION OF THE FREEZING POINT

If a dissolved substance is dissociated in solution to the degree α , each molecule forming n ions, it has been shown that the number of gram molecules resulting from each gram molecule of solute taken $= 1 + (n-1)\alpha$. The depression of the freezing point is proportional to the number of gram molecules in unit volume, so that if d_0 = the observed freezing point depression, and d_1 = the depression if no dissociation occurred,

$$d_0 = (1 + (n-1)\alpha) \times d_1$$

Hence,

$$\frac{\text{molecular weight for no dissociation}}{\text{observed molecular weight}} = 1 + (n-1)\alpha = i$$

Example. The freezing point of a solution of 0.3015 gm. of silver nitrate in 28.40 gm. of water is depressed by 0.212° . To what extent is the silver nitrate dissociated?

100 gm. of water contain $\frac{100}{28.40} \times 0.3015$ gm. of AgNO_3 ,

$\frac{100}{28.40} \times 0.3015$ gm. AgNO_3 in 100 gm. of water give a depression of 0.212°

$\therefore \frac{100}{28.40} \times 0.3015 \times \frac{18.5}{0.212}$ gm. of AgNO_3 in 100 gm. of water would give a depression of 18.5°

$$\therefore \text{apparent molecular weight} = \frac{100}{28.40} \times 0.3015 \times \frac{18.5}{0.212} = 93.15.$$

Molecular weight of undissociated $\text{AgNO}_3 = 169.9$

From the formula above, $\frac{169.9}{93.15} = 1 + (n-1)\alpha$

For AgNO_3 , $n = 2$.

$$\therefore \alpha = \frac{169.9}{93.15} - 1 = 0.826$$

i.e., the silver nitrate is 82.6% dissociated.

Certain substances have the converse property of *associating* in solution. An example of this type is benzoic acid, $\text{C}_7\text{H}_6\text{O}_2$, which in solution in benzene associates to some extent to double molecules $(\text{C}_7\text{H}_6\text{O}_2)_2$. If

n molecules of the simple substance associate to form each larger molecule, and if a fraction x be associated, in place of each gram molecule of original solute there are $(1-x)$ gm. mols. unassociated and $\frac{x}{n}$ gram molecules of associated substance, i.e., $1-x(1-\frac{1}{n})$ gm. mols. altogether.

Hence $\frac{\text{observed freezing point depression.}}{\text{freezing point depression for no association}}$
 $= 1 - x(1 - \frac{1}{n})$. i.e., $\frac{\text{Mol. wt. for single mols.}}{\text{Observed mol. wt.}} = 1 - x(1 - \frac{1}{n})$

Example. Phenol, C_6H_5O , associates in water to double molecules. A solution of 0.6677 gm. of phenol in 35.5 gm. of water has a freezing point depression of 0.215° . Find the degree of association of the phenol.

Substituting in the formula $M = \frac{w}{l} \times K$

$$\text{Apparent molecular weight} = \frac{100}{35.50} \times 0.6677 \times \frac{18.5}{0.215} = 162.6$$

$$\frac{\text{Mol. wt. of simple molecules}}{\text{Observed mol. wt.}} = \frac{94}{162.6} = 1 - x(1 - \frac{1}{2}),$$

since $n = 2$.

$$\text{i.e., } \frac{1}{2}x = 1 - 0.578$$

$$\text{or } x = 2 \times 0.422 = 0.844$$

Hence the phenol is 84.4% associated.

PROBLEMS ON THE DETERMINATION OF MOLECULAR WEIGHTS BY THE DEPRESSION OF THE FREEZING POINT

(The answers to problems with odd numbers will be found at the end of the book)

- 276 The solution of 0.2257 gm. of sulphur chloride in 23.7 gm. of benzene brought about a freezing point depression of 0.362° . Calculate the molecular weight of sulphur chloride.
- 277 A solution of 1.353 gm. of sulphur in 67 gm. of naphthalene has its freezing point lowered 0.542° . The depression constant of naphthalene is 69° per 100 gm. Of how many atoms of sulphur is the sulphur molecule composed?

- 278 A freezing point depression of 0.567° is brought about when 0.440 gm. of anthracene is dissolved in 22.2 gm. of benzene. Find the molecular weight of anthracene.
- 279 The freezing point lowering of a solution of 0.506 gm. of tellurium tetrabromide in 37.5 gm. of glacial acetic acid was 0.116° . Calculate the molecular weight of the compound.
- 280 If the solution of 1.07 gm. of silver nitrate in 100 gm. of water has its freezing point depressed 0.211° , calculate the degree of dissociation of the silver nitrate.
- 281 A solution of 0.453 gm. of calcium chloride in 25 c.c. of water has its freezing point depressed 0.808° . Calculate the factor i and the degree of ionisation of the calcium chloride.
- 282 A freezing point depression of 0.470° is produced by the solution of 0.218 gm. of potassium chloride in 21 c.c. of water. Find the degree of ionisation of the potassium chloride.
- 283 Phenol associates in benzene to double molecules. The solution of 1 gm. of phenol in 50 gm. of benzene has its freezing point depressed 0.690° . To what degree is the phenol associated?
- 284 If the solution of 0.197 gm. of camphor ($C_{10}H_{16}O$) in 20 gm. of solvent has its freezing point depressed by 0.332° , what is the depression constant for the solvent used?

DETERMINATION OF MOLECULAR WEIGHTS BY THE ELEVATION OF THE BOILING POINT

The effect of dissolved substances is to raise the boiling point of a solution above that of the pure solvent. Both elevation of the boiling point and depression of the freezing point are actually the consequences of the action of the solute in lowering the vapour pressure of the solvent, and accordingly are governed by the same laws. Exactly as for freezing point depression, Raoult found that for any given solute, the boiling point elevation is proportional to the concentration of the solution, and for any one solvent the boiling point elevation is the same for equimolecular solutions of different solutes. The determination of boiling point elevation is attended with greater difficulties than is the measurement of freezing point depression, and is probably less frequently employed in consequence. In particular, it is difficult to determine the true temperature of the boiling solution,

and not that of condensing vapour, and at the same time to avoid superheating. For the various modifications of procedure employed in the Beckmann, Cottrell and Landsberger methods the student is referred elsewhere.

As in the case of freezing point depression, for each solvent a *molecular boiling point elevation* per 100 gm. of solvent is recorded, being the elevation in boiling point which would be produced by dissolving one gram molecule of substance in 100 gm. of solvent. Since the boiling point of a liquid varies markedly with the barometric pressure, the molecular elevation constant varies slightly also. Unless otherwise stated, all values refer to determinations at 760 mm. pressure.

If the molecular elevation constant = K' , and a solution contains w gm. of solute of molecular weight M per 100 gm. of solvent, the boiling point elevation

$$e = \frac{w}{m} \times K'. \quad \text{i.e., } M = \frac{w}{e} \times K'.$$

For some frequently used solvents, the elevation constants are:—

water	5.2°
benzene	26.1°
chloroform	39.0°
acetone	17.2°

Example. A solution of 0.5143 gm. of anthracene in 35.0 gm. of chloroform has its boiling point raised by 0.323°. Calculate the molecular weight of anthracene.

Weight of anthracene in 100 gm. of chloroform

$$= \frac{100}{35.0} \times 0.5143 \text{ gm.}$$

An elevation of 0.323° is produced by $\frac{100}{35.0} \times 0.5143$ gm. of

anthracene in 100 gm.

$$\therefore \text{ " " } 39.0^\circ \text{ " " } \frac{100}{35.0} \times 0.5143 \times \frac{39}{0.323} \text{ gm.}$$

= 177.4 gm. in 100 gm. chloroform. \therefore molecular weight = 177.4.
(calculated from the formula, 178).

PROBLEMS ON THE DETERMINATION OF MOLECULAR WEIGHTS BY THE ELEVATION OF THE BOILING POINT

(The answers to problems with odd numbers will be found at the end of the book)

In all cases, the figures refer to determinations at 760 mm. barometric pressure.

- 285 The solution of 2.78 gm. of benzophenone in 55.6 gm. of acetone had its boiling point raised by 0.472° . Find the molecular weight of benzophenone.
- 286 A boiling point elevation of 0.483° was shown by the solution of 0.97 gm. of a hydrocarbon in 31.6 gm. of benzene. Calculate the molecular weight of the hydrocarbon.
- 287 By dissolving 0.517 gm. of nitrogen sulphide in 36.5 gm. of chloroform, the boiling point was raised 0.300° . Nitrogen sulphide contains 69.5% sulphur, 30.5% nitrogen. Find the molecular formula of the compound.
- 288 A boiling point elevation of 0.059° was produced by dissolving 0.1235 gm. of chromium carbonyl in 24.1 gm. of benzene. What is the molecular weight of chromium carbonyl?
- 289 If the boiling point of water was raised 0.071° by dissolving 2.35 gm. of sucrose ($C_{12}H_{22}O_{11}$) in 50 gm., calculate the molecular elevation constant for water.
- 290 The molecule of iodine contains two atoms. If the boiling point of a solution of 2.06 gm. of iodine in 30.14 gm. of ether was raised 0.566° , calculate the elevation constant per 100 gm. of ether.

CHAPTER VI

VOLUMETRIC ANALYSIS

THE EQUIVALENT WEIGHTS OF COMPOUNDS

The concept of the equivalent weights of compounds originated in a study of the formation of salts by the neutralisation of acids by bases and, as early as 1767, Cavendish termed those weights of potash and marble that neutralised the same weight of acid, *equivalent*.

The equivalent weight of a metallic element has been defined as that weight which will liberate 1.008 gm. of hydrogen from an acid. It is immaterial what acid is used, but the weight of acid which contains the 1.008 gm. of hydrogen capable of being replaced by a metal will be different with different acids. Thus 36.46 gm. of hydrochloric acid and 63.01 gm. of nitric acid each contain the equivalent weight of hydrogen replaceable by an equivalent weight of a metal. It is legitimate, therefore, to regard 36.46 and 63.01 as the equivalent weights of hydrochloric and nitric acid respectively. Again, when an equivalent weight (36.46) of hydrochloric acid is treated with a metal (e.g., zinc), an equivalent weight of hydrogen is evolved and an equivalent weight of zinc chloride ($35.46 + 32.69 = 68.15$) formed, by replacing the hydrogen by an equivalent weight of zinc (32.69).

The equivalent of a simple compound such as a hydride, an oxide or a chloride may be defined as that weight of the compound that contains an equivalent of reactive hydrogen (1.008), an equivalent of oxygen (8) or an equivalent of chlorine (35.46).

The equivalent weight of an acid is that weight which contains one equivalent of hydrogen replaceable by a

metal (or which gives rise to one equivalent weight of hydrogen ion); the equivalent of a base is that weight which will neutralise one equivalent of an acid (or which gives rise to one equivalent weight of hydroxyl ion).

The equivalents of more complicated compounds may be found by a study of their formulæ, or of an equation which represents their reaction with some compound of known equivalent weight. Take, for example, sodium carbonate, Na_2CO_3 . The formula indicates that the compound is formed from the acid H_2CO_3 by replacement of the two hydrogen atoms by sodium. The equivalent of the acid would be, by definition, that weight which contained one equivalent weight of replaceable hydrogen (*i.e.*, half the molecular weight); similarly the equivalent of the salt will be that weight which contains one equivalent of sodium (or half its molecular weight). The same conclusion will be reached by considering the reaction:— $\text{Na}_2\text{CO}_3 + 2\text{HCl} = 2\text{NaCl} + \text{CO}_2 + \text{H}_2\text{O}$. One molecular weight of the carbonate reacts with two molecular weights of hydrochloric acid, that is to say, with two equivalents of hydrochloric acid; hence half the molecular weight of the carbonate will be its equivalent weight, as that is the weight which reacts with one equivalent of hydrochloric acid.

The equivalents of compounds reacting in such a way as to cause a change in valency in one of the essential elements concerned are determined by considering the change in valency. For example, in the reaction:—



the equivalent of phosphorus trichloride is half its molecular weight, as one molecular weight of the compound reacts with two equivalents of chlorine. It is the change in valency (in this case from 3 to 5) that determines the equivalent, and not the absolute value of the valency. In such reactions where there is a change in valency, the equivalent of the reacting compound is defined as that weight which undergoes a unit valency change. Thus in the example above, one molecule of PCl_3 has a change of valency = 2, therefore half a molecular weight will

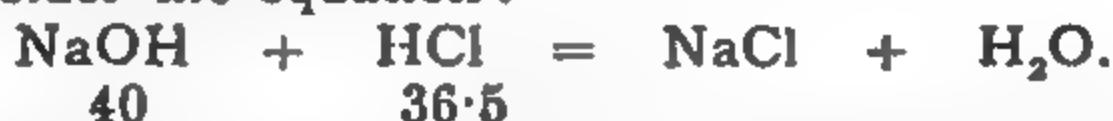
have a unit valency change and so the equivalent is half the molecular weight. Similarly in the case of the oxidation of ferrous compounds to ferric compounds:—



ferrous iron has valency = 2, ferric iron = 3, the change in valency per molecule being therefore one; the equivalent is thus the same as the molecular weight. (For application of this, see p. 124).*

NORMAL SOLUTIONS

Consider the equation:—



It follows that 40 gm. of caustic soda neutralise 36.5 gm. of hydrochloric acid. Now, if we dissolved the 40 gm. of caustic soda in water so as to make up a litre of solution, and diluted the hydrochloric acid to one litre, we should find that the litre of acid exactly neutralised the litre of alkali, or that 1 c.c. of the acid neutralised 1 c.c. of the alkali. Such a solution which contains one gram equivalent weight of a substance in one litre of solution is known as a *normal* solution.

A given volume of a *normal* solution of any acid will neutralise the same volume of a *normal* solution of any alkali, as the given volume of normal solution, whether acid or alkali, will always contain the same fraction of an equivalent of acid or alkali. Thus 20 c.c. of normal caustic soda solution will neutralise, or will be equivalent to (\equiv) 20 c.c. of normal HNO_3 (written $N \text{HNO}_3$), 20 c.c. $N \text{H}_2\text{SO}_4$, 20 c.c. $N \text{H}_3\text{PO}_4$ or 20 c.c. of any other N acid.

In the equation:—



it will be seen that 2×40 gm., or two litres of normal solution of caustic soda will neutralise one molecular weight (98 gm.) of sulphuric acid. One equivalent

* Note that the equivalent of any substance can be defined only with respect to the particular reaction under consideration.

weight (40 gm.) or one litre of normal solution of caustic soda will thus neutralise $\frac{98}{2} = 49$ gm. of sulphuric acid.

A normal solution of sulphuric acid will therefore contain 49 gm. per litre, which, as we would expect from the definition, is the equivalent weight of the acid, as there are two atoms of replaceable hydrogen in its molecule.

The equivalent weight (which contains 1 equivalent of replaceable hydrogen) of a dibasic acid is thus half its molecular weight (which contains 2 equivalents of replaceable hydrogen); the equivalent weight of a monobasic acid (*e.g.*, HCl in the equation above) is the same as its molecular weight and the equivalent weight of a tribasic acid is one-third of its molecular weight. It is convenient to remember, too, that the equivalent weight of any base will be its molecular weight divided by the number of hydroxyl groups it contains.

Thus :—

$$\text{the equivalent weight of KOH} = \frac{39+16+1}{1} = 56$$

$$\text{the equivalent weight of Ba(OH)}_2 = \frac{137.5+(2 \times 17)}{2} = 85.75$$

$$\text{the equivalent weight of Al(OH)}_3 = \frac{27+(3 \times 17)}{3} = 28$$

For many analytical purposes normal solutions are too concentrated, so decinormal ($N/10$) solutions which contain a tenth of an equivalent weight per litre are often used. Other solutions, occasionally employed, are semi-normal ($N/2$) solutions, containing half an equivalent weight per litre and centinormal $N/100$ solutions that contain one-hundredth of an equivalent weight per litre. The volumes of any of these solutions that react with one another should now be quite clearly understood, *e.g.*,

$$1 \text{ litre } N \text{ HCl} \equiv 1 \text{ litre } N \text{ NaOH} \equiv 1 \text{ litre } N \text{ H}_2\text{SO}_4$$

$$10 \text{ c.c. } N/10 \text{ HCl} \equiv 10 \text{ c.c. } N/10 \text{ NaOH} \equiv 1 \text{ c.c. } N \text{ H}_2\text{SO}_4$$

$$100 \text{ c.c. } N/100 \text{ HCl} \equiv 10 \text{ c.c. } N/10 \text{ NaOH} \equiv 1 \text{ c.c. } N \text{ H}_2\text{SO}_4$$

$$50 \text{ c.c. } N/50 \text{ HCl} \equiv 1 \text{ c.c. } N \text{ NaOH} \equiv 2 \text{ c.c. } N/2 \text{ H}_2\text{SO}_4$$

This is the basis of volumetric analysis, in which solutions of known normality are made to react with solutions

of unknown concentration, the volume of the solution of known concentration required to react with a definite volume of the solution of unknown strength being determined. The ratio of the reacting volumes thus gives the concentration of the unknown solution in terms of that of known normality.

In practice the solutions used in volumetric analysis are seldom exactly N , exactly $N/10$, etc. It is quite unnecessary to make them so, a small factor being placed before the normality sign to indicate the deviation from strict normality (or from decinormality, etc.). Thus a solution of NaOH labelled $1.018 N$, contains 1.018 equivalents of NaOH per litre $= 1.018 \times 40$ gm. Similarly a $.973 N/10$ solution will contain $.0973$ equivalents per litre; in general a solution of strength $x N$ contains x equivalents per litre.

10 c.c. of a $.93 N$ solution $\equiv .93 \times 10 = 9.3$ c.c. of N solution

100 c.c. of a $1.14 N/10$ solution $\equiv 1.14 \times 100 = 114$ c.c. of $N/10$ solution.

Example. What is the concentration in grams per litre of a $.97 N/10$ solution of (a) caustic potash and (b) barium hydroxide; also how many c.c. of $1.1 N \text{HCl}$ will 20 c.c. of either of these solutions neutralise?

(i) a $.97 N/10$ solution contains 0.097 gram equivalents per litre
 $= 0.097 \times \text{the equivalent weight per litre.}$

(a) caustic potash (KOH) contains 1 OH group

$$\therefore \text{equivalent weight} = \frac{39+16+1}{1} = 56$$

(b) barium hydroxide (Ba(OH)_2) contains 2 OH groups

$$\therefore \text{equivalent weight} = \frac{137.5+(2 \times 17)}{2} = 85.75$$

\therefore concentration of KOH solution is $0.097 \times 56 = 5.43$ grams per litre and concentration of Ba(OH)_2 solution is $0.097 \times 85.75 = 8.32$ grams per litre.

(ii) 20 c.c. of $.97 N/10 \equiv 20 \times .97$ c.c. $= 19.4$ c.c. $N/10$ solution

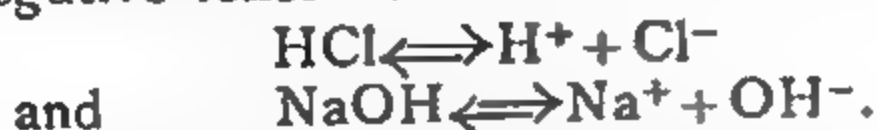
$$\equiv \frac{19.4}{10} \text{ c.c. } N \text{ solution}$$

$$\equiv \frac{19.4}{10 \times 1.1} \text{ c.c. } 1.1 N \text{ solution}$$

$$= 1.76 \text{ c.c.}$$

NEUTRALISATION

In the previous chapter it was stated that acids and alkalies split up in aqueous solution into positive and negative ions. Thus:—



When an acid reacts with a base, a salt and water are formed, *e.g.*, $\text{HCl} + \text{NaOH} = \text{NaCl} + \text{H}_2\text{O}$.

The salt is also an electrolyte and will exist in solution in the ionic condition:— $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$.

All the reactants except water (which is ionized to a very small extent) exist in solution in ionic form and so the neutralisation of an acid by a base to form a salt must primarily be the combination of a hydrogen ion with a hydroxyl ion to form water $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$.

That this is the fundamental reaction which takes place when any acid reacts with a base, is shown by the fact that the amount of heat given out when equivalent amounts of any strong acid and any strong base react is always approximately the same.

The *strength* of an acid is governed by the extent of its dissociation into ions—by the number of hydrogen ions produced by a given amount of acid. HCl and HNO_3 are strong acids, being largely dissociated and thus giving rise to a high hydrogen ion concentration. Acetic acid, CH_3COOH , is a weak acid as it is only dissociated to a small extent, and thus produces only a small concentration of hydrogen ions.

INDICATORS

In order to tell when the neutralisation of a base by an acid is complete, a small amount of a coloured substance called an indicator is added, which changes colour when the end-point of the titration is reached. As the neutralisation really means the removal of hydroxyl ion by hydrogen ion, or of hydrogen ion by hydroxyl ion, the indicator by its colour change shows the presence of excess hydrogen ions or of excess hydroxyl ions. Indicators are either weak acids or weak bases whose ions

are of a different colour from the undissociated molecules. Some indicators are more sensitive to the hydrogen ion than others, *i.e.*, they require a small hydrogen ion concentration to make them change colour.

Methyl Orange is one of the commonest indicators in use. It is yellow in alkaline, and red in acid solution. It is not very sensitive to the hydrogen ion and requires quite a large hydrogen ion concentration before it will change colour, hence it cannot be used for the titration of weak acids. It can, however, be used in the titration of carbonates with acids, as the presence of carbonic acid does not affect it.

Litmus is more sensitive to the hydrogen ion than methyl orange, and so cannot be used in the presence of CO_2 . It is seldom used in quantitative work.

Phenolphthalein, which is deep red in alkaline solution and colourless in acid solution, is extremely sensitive to the hydrogen ion and will become colourless even in the presence of small concentrations. It can therefore be used in the titration of weak acids which are dissociated to a very small extent.

Methyl Red is the only indicator that can be conveniently used in the presence of ammonia.

ACID-ALKALI TITRATIONS

Although the methods of volumetric analysis can be applied to any reactions which take place in aqueous solution, the calculation of the results is the same in all cases as the calculation of acid-alkali titration results. There are four main types of calculation which will now be illustrated, each by an example of an acid-alkali titration. Further calculations illustrating special types of reaction will then be worked, when it will be seen that the same principles apply throughout.

The use of normalities is the simplest, quickest and only logical method of calculating the results of volumetric analysis. On no account must the amounts of the reacting substances be worked out by calculat-

ing the weight of material in a solution of known normality and applying this in the chemical equation.

I. STANDARDISATION OF A SOLUTION OF UNKNOWN STRENGTH BY TITRATING IT WITH A WEIGHED AMOUNT OF MATERIAL DISSOLVED IN WATER

As most acids are sold in solutions of variable concentration, a solution of approximately the required strength is made up and standardised by running a measured volume of it from a burette into a flask which contains a weighed amount of anhydrous sodium carbonate.

Example. A solution of HCl was standardised by titration against anhydrous sodium carbonate. It was found that 0.197 grams of Na_2CO_3 required 36.7 c.c. of acid for neutralisation, using methyl orange as indicator. Determine the normality of the acid.

By definition, an equivalent weight of sodium carbonate will react with 1000 c.c. of N acid,

Or 53 gm. $\text{Na}_2\text{CO}_3 \equiv 1000$ c.c. of N HCl

$\therefore 0.197$ " " $\equiv \frac{1000 \times 0.197}{53}$ c.c. N HCl

but 0.197 " " $\equiv 36.7$ c.c. of x N HCl

This means that 36.7 c.c. of x N HCl $\equiv 1000 \times \frac{0.197}{53}$ c.c. N HCl

$$\therefore \text{Normality} = 1000 \times \left(\frac{0.197}{53} \right) \times \frac{1}{36.7} = 0.1013$$

\therefore Solution is 0.1013 N or 1.013 $N/10$.

It should be noted that the normality factor is given by the ratio of the calculated volume of normal reagent to the volume (36.7 c.c.) actually required.

II. DETERMINATION OF THE STRENGTH OF A SOLUTION OF UNKNOWN CONCENTRATION BY TITRATION WITH A SOLUTION OF KNOWN CONCENTRATION

A definite volume of the solution of unknown concentration is measured out and after the addition of a few drops of indicator the solution of known concentration is run in until the end point is reached, when its volume is read.

Example. The concentration of an ammonia solution was determined by titration with a .963 *N*/10 solution of sulphuric acid. It was found that 25.0 c.c. of the ammonia solution required 27.1 c.c. of the standard acid for neutralisation. Calculate (a) the normality of the ammonia solution and (b) its concentration expressed as grams of ammonium hydroxide per litre.

(a) 25 c.c. of ammonia solution \equiv 27.1 c.c. of .963 *N*/10 H_2SO_4

1 c.c. of ammonia solution $\equiv \frac{27.1}{25.0} \times .963$ c.c. of *N*/10 H_2SO_4

but 1 c.c. of *N*/10 ammonia solution \equiv 1 c.c. *N*/10 H_2SO_4

\therefore Normality of the solution $= \frac{27.1}{25.0} \times .963$ *N*/10

$= .99$ *N*/10 or 0.099 *N*

(NOTE.—The concentration of the unknown solution is always the ratio of the volume of standard solution required to that of unknown solution taken, multiplied by the normality of the standard solution.)

(b) The normality of a solution of a substance \times its equivalent weight gives the concentration of the solution in grams per litre.

The equivalent weight of NH_4OH is the same as its molecular weight ($14+4+17=35$) as it contains only 1 hydroxyl group.

\therefore The concentration of the solution $= .99 \times \frac{35}{10} = 3.465$ gm.

per litre.

III. DETERMINATION OF THE PERCENTAGE COMPOSITION OF A SUBSTANCE BY WEIGHING OUT A DEFINITE QUANTITY, DISSOLVING IN WATER AND DILUTING TO A DEFINITE VOLUME IN A MEASURING FLASK, THEN TITRATING DEFINITE VOLUMES OF THIS SOLUTION WITH A STANDARD SOLUTION.

This is really a practical extension of the previous case, the unknown solution being made up by weighing out a definite amount of material. The true weight of substance present being determined by titration, its percentage in the original substance can be calculated.

Example. 3.712 grams of sodium carbonate crystals were weighed out, dissolved in water and made up to 250 c.c. Three successive samples of 25 c.c. of this solution required 28.05

c.c., 27.90 c.c. and 27.90 c.c. respectively, for titration with .93 N/10 H_2SO_4 , using methyl orange as indicator. Calculate the percentage of Na_2CO_3 in the crystals.

Average volume of sulphuric acid required = 27.95 c.c.
 \therefore 25.00 c.c. $\text{Na}_2\text{CO}_3 \equiv 27.95$ c.c. .93 N/10 H_2SO_4
 hence, as in the previous example, the normality of the carbonate solution is $\frac{27.95}{25.00} \times .93$ N/10.

and the concentration is $\frac{27.95}{25.00} \times .93 \times \frac{\text{equivalent weight } \text{Na}_2\text{CO}_3}{10}$
 $= \frac{27.95}{25.00} \times .93 \times \frac{53}{10}$ gm. litre.

and the weight in 250 c.c. will be $\frac{27.95}{25.00} \times .93 \times \frac{53}{10} \times \frac{1}{4}$ grams
 but 3.712 gm. of the crystals were dissolved in 250 c.c.

\therefore they contain $\frac{27.95}{25.00} \times .93 \times \frac{53}{10} \times \frac{100}{3.712 \times 4} \% \text{Na}_2\text{CO}_3$
 $= 37.14 \% \text{Na}_2\text{CO}_3$

IV. DETERMINATION OF THE QUANTITY OF A MATERIAL BY ADDING IT TO A KNOWN VOLUME (IN EXCESS) OF STANDARD SOLUTION OF A REAGENT WITH WHICH IT WILL REACT AND TITRATING THE RESIDUAL AMOUNT OF REAGENT WITH A STANDARD SOLUTION OF ANOTHER REAGENT

Example. In the determination of the percentage of ammonia in a salt the following data were obtained:—1.361 gm. of the salt were boiled with caustic soda and the ammonia evolved passed into 75 c.c. of a 1.02 N/2 solution of sulphuric acid. After the ammonia evolution was finished the excess acid was determined by titration with 1.27 N/2 NaOH solution, 23.14 c.c. being required. Determine the percentage of ammonia in the salt.

The ammonia liberated would neutralise an equivalent amount of acid.

As the total amount of acid at the beginning of the analysis is known and the amount left (in excess of that neutralised by the ammonia) estimated by titration, the ammonia liberated will be equivalent to the difference between these two volumes. In order to compare these volumes, they must all be reduced to the same normality.

Initial volume of acid = 75 c.c. of 1.02 $N/2$ H_2SO_4 = $75 \times \frac{1.02}{2}$
c.c. $N H_2SO_4$

$$= 38.50 \text{ c.c. } N H_2SO_4$$

Volume of 1.27 N $NaOH$ required to neutralise excess acid =
23.14 c.c.

$$= 23.14 \times \frac{1.27}{2} \text{ c.c. } N NaOH$$

$$= 14.70 \text{ c.c. } N NaOH$$

$$14.70 \text{ c.c. } N NaOH \equiv 14.70 \text{ c.c. } N H_2SO_4$$

\therefore Excess acid is equivalent to 14.70 c.c. of normal solution.

\therefore Volume of N acid used up by the
ammonia = $38.50 - 14.70 = 23.80$ c.c.

$$\equiv 23.80 \text{ c.c. } N NH_3 \text{ solution.}$$

$$\equiv \frac{23.80}{1000} \text{ equivalents of } NH_3$$

$N NH_3$ solution contains 17 gm. per litre

$$\therefore \text{ weight of } NH_3 = \frac{23.8 \times 17}{1000} \text{ gm.}$$

$$\therefore \text{ ammonia in the salt} = \frac{23.8 \times 17}{1000} \times \frac{100\%}{1.361}$$

$$= 29.7\%$$

DETERMINATION OF STRONG ALKALIES AND CARBONATES IN MIXTURES (THE USE OF TWO INDICATORS)

When caustic soda or caustic potash is brought into contact with the air, a certain amount of carbon dioxide is absorbed by the hydroxide with the formation of sodium (or potassium) carbonate.

It is convenient, therefore, to have a quick method of determining both the hydroxide and the carbonate in a single sample of such a mixture. This is done by the titration of a given volume of the solution with a strong acid, using phenolphthalein as indicator and when the end point is reached, adding methyl orange and determining the second end point.

Sodium hydroxide is a strong base, that is to say it dissociates almost completely to sodium ions and to

hydroxyl ions. In titrating it with a strong acid such as hydrochloric acid, therefore, the end point as shown by either methyl orange or phenolphthalein will indicate the complete neutralisation of the hydroxide.

Let us now consider the neutralisation of sodium carbonate solution by hydrochloric acid in the presence of phenolphthalein and of methyl orange respectively. The reaction takes place in two stages:—



During the first stage there are produced only NaHCO_3 and NaCl , neither of which gives rise to hydrogen ions; so that even phenolphthalein, which is a very sensitive indicator, will not change colour during this part of the reaction.

As soon as the first stage is exactly completed (i.e., when the carbonate is half neutralised) the next drop of HCl will produce some free carbonic acid which will ionise to a small extent, although it is a weak acid:—



As phenolphthalein is extremely sensitive to the hydrogen ion, it will change colour even in the presence of the weak acid and so the solution will become colourless immediately the first trace of H_2CO_3 is formed, that is when the neutralisation is half completed. Methyl orange, which is not as sensitive as phenolphthalein, is not affected by the small concentration of hydrogen ions formed by the weak carbonic acid and so will not give an end point until the second stage of the reaction has gone to completion and there is a trace of the strong acid, $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$, present, which will give a sufficiently high hydrogen ion concentration to change the colour of the methyl orange.

If we have a mixture of sodium hydroxide and sodium carbonate and titrate it with hydrochloric acid in the presence of phenolphthalein, the end point will be reached when all the hydroxide is neutralised and half the carbonate. If now methyl orange is added, more acid can be run in until the end point of the titration (using methyl

orange) is reached when all the hydroxide and all the carbonate is neutralised.

The difference of volume between these two titrations will thus be equivalent to half the carbonate present.

M.O. gives Hydroxide + carbonate.

P.P. gives Hydroxide + $\frac{1}{2}$ carbonate.

M.O. - P.P. gives $\frac{1}{2}$ carbonate.

Example. 28.17 grams of commercial caustic potash were dissolved in water and the solution diluted to 1 litre. 50 c.c. of the dilute solution were titrated with a 0.498 N solution of HCl. Using phenolphthalein 41.9 c.c. were required, and using methyl orange, 42.95 c.c. Calculate the % composition of the sample.

$$\begin{array}{rcl}
 \text{M.O.} & = & \text{hydroxide} + \text{carbonate} & = & 42.95 \text{ c.c.} \\
 \text{P.P.} & = & \text{hydroxide} + \frac{1}{2} \text{ carbonate} & = & 41.90 \text{ c.c.} \\
 & & & & \hline
 \text{M.O.} - \text{P.P.} & = & \frac{1}{2} \text{ carbonate} & = & 1.05 \text{ c.c.} \\
 & & & & \hline
 \therefore \text{total carbonate} & & & = & 2.10 \text{ c.c.} \\
 \text{Total hydroxide} + \frac{1}{2} \text{ carbonate} & & & = & 41.90 \text{ c.c.} \\
 \frac{1}{2} \text{ carbonate} & & & = & 1.05 \text{ c.c.} \\
 & & & & \hline
 \therefore \text{total hydroxide} & & & = & 40.85 \text{ c.c.} \\
 & & & & \hline
 \end{array}$$

Calculation of % KOH.

50 c.c. KOH \equiv 40.85 c.c. of 0.498 N HCl

\therefore solution is $\frac{40.85}{50} \times 0.498$ N with respect to KOH

\therefore it contains $\frac{40.85}{50} \times 0.498 \times 56$ gm. per litre.

$$\begin{aligned}
 \therefore \% \text{ KOH} &= \frac{40.85}{50} \times 0.498 \times 56 \times \frac{100}{28.17} \\
 &= 79.2 \%
 \end{aligned}$$

Calculation of % K_2CO_3

50 c.c. $\text{K}_2\text{CO}_3 \equiv$ 2.10 c.c. of 0.498 N HCl

\therefore solution is $\frac{2.10}{50} \times 0.498$ N with respect to K_2CO_3

\therefore it contains $\frac{2.10}{50} \times 0.498 \times 69$ gm. per litre

$$\begin{aligned}
 \therefore \% \text{ K}_2\text{CO}_3 &= \frac{2.10}{50} \times 0.498 \times 69 \times \frac{100}{28.17} \\
 &= 5.02 \%
 \end{aligned}$$

29.10.19

The sample contains 79.2% KOH, 5.02% K_2CO_3 ,
and (by difference) 15.78% H_2O .

The method of calculation in this case is, in essential, the same as method III on page 118.

DETERMINATION OF EQUIVALENT WEIGHTS BY VOLUMETRIC ANALYSIS

Example. 0.366 grams of an organic acid were dissolved in 150 c.c. of .98 $N/10$ NaOH solution and the excess of caustic soda titrated with a 1.034 $N/10$ H_2SO_4 solution, 47.80 c.c. being required. Calculate the equivalent weight of the acid.

$$\begin{aligned} 150 \text{ c.c. of } .98 \text{ } N/10 \text{ NaOH solution} &\equiv \frac{150 \times .98}{10} \text{ c.c. of } N \text{ solution} \\ &= 14.7 \text{ c.c.} \end{aligned}$$

$$\begin{aligned} 47.8 \text{ c.c. of } 1.034 \text{ } N/10 \text{ } H_2SO_4 \text{ solution} &\equiv \frac{47.8 \times 1.034}{10} \text{ c.c. of } N \\ \text{solution} &= 4.94 \text{ c.c.} \end{aligned}$$

the acid will be equivalent to the caustic soda neutralised
 $= 14.70 - 4.94 = 9.76$ c.c. of N solution.

Hence 9.76 c.c. of N solution contain 0.366 gm. of the acid

$$\begin{aligned} \therefore 1000 \text{ c.c. of } N \text{ } \quad \quad \quad &\frac{0.366 \times 1000}{9.76} \text{ gm.} \\ &= 37.5 \text{ gm.} \end{aligned}$$

But, by definition, the equivalent weight of a substance is contained in 1000 c.c. of its normal solution, hence 37.5 is the equivalent weight of the acid.

A similar method may be used to determine the equivalent of a metal by dissolving a known weight of its oxide in a known volume of standard acid and determining the excess acid by titration with standard alkali.

Example. 0.288 gm. of cadmium oxide were dissolved in 50 c.c. of 1.01 $N/10$ sulphuric acid, the residual acid requiring 6.21 c.c. of .92 $N/10$ caustic soda for titration. Calculate the equivalent weight of cadmium.

$$\begin{aligned} 50 \text{ c.c. of } 1.01 \text{ } N/10 \text{ sulphuric acid} &\equiv 50 \times 1.01 \text{ c.c. } N/10 \text{ acid} \\ &= 50.50 \text{ c.c.} \end{aligned}$$

$$\begin{aligned} 6.21 \text{ c.c. of } .92 \text{ } N/10 \text{ alkali} &\equiv 6.21 \times .92 \text{ c.c. } N/10 \text{ alkali} = 5.61 \text{ c.c.} \\ \therefore \text{The acid used up by the cadmium oxide} &\equiv 50.50 - 5.61 \text{ c.c.} \\ &= 44.89 \text{ c.c. of } N/10 \text{ solution} \end{aligned}$$

44.89 c.c. of $N/10$ acid $\equiv 0.288$ gm. of oxide

\therefore 10000 c.c. of $N/10$ acid $\equiv 0.288 \times \frac{10000}{44.89}$ gm. of oxide.
 $= 64.15$ gm.

But 10000 c.c. of $N/10$ acid $\equiv 1000$ c.c. N acid $\equiv 1$ equivalent
of cadmium oxide
 $= 64.15$ gm.

The above calculations are a direct application of method IV on page 119.

ANALYSIS BY MEANS OF OXIDISING AGENTS

In many reactions in which oxidation takes place, the extent of oxidation may be used as a measure of the amount of oxidisable material present, since, by definition, one equivalent weight of substance will be oxidised by one equivalent weight of oxygen. As the oxygen is usually produced by an oxidising agent we define the equivalent weight of the oxidising agent as that weight which will give rise to one equivalent, $= 8$ grams (the equivalent weight), or $22.41 \div 4 = 5.6025$ litres (the equivalent volume) of oxygen available for oxidation.

Let us consider the oxidation of ferrous compounds to ferric compounds:—

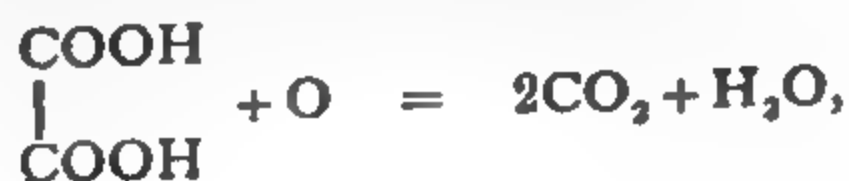


or in the case of a salt:—



It will be seen from the equations that one atomic weight of oxygen (16 gm.) oxidises two molecules of a ferrous compound and hence one equivalent weight of oxygen (8 gm.) will oxidise one molecule of a ferrous compound. Hence for purposes of oxidation titrations, the equivalent weights of ferrous oxide and ferrous sulphate will be the same as their molecular weights and one equivalent (or molecular) weight of a ferrous compound will be oxidised by one litre of normal solution of an oxidising agent.

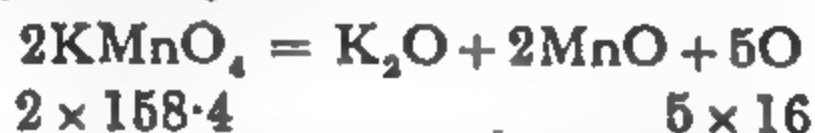
Again in the case of oxalic acid:—



one atom of oxygen (16 grams) oxidises one molecule of the acid, and so one equivalent (8 grams) will oxidise half the molecular weight. Hence the equivalent weight of oxalic acid will be half of its molecular weight and will be oxidised by 1 litre of normal solution of an oxidising agent. By similar considerations the equivalent weight of any other material to be oxidised may be calculated.

NORMAL SOLUTIONS OF OXIDISING AGENTS

Potassium permanganate is the oxidising agent most extensively used for titrations involving oxidation. It oxidises, *e.g.*, ferrous sulphate and oxalic acid, mentioned above, and may be used for estimating the quantities of these substances present in solutions of unknown concentration. The reaction by means of which potassium permanganate gives up its oxygen for oxidation may be expressed:—

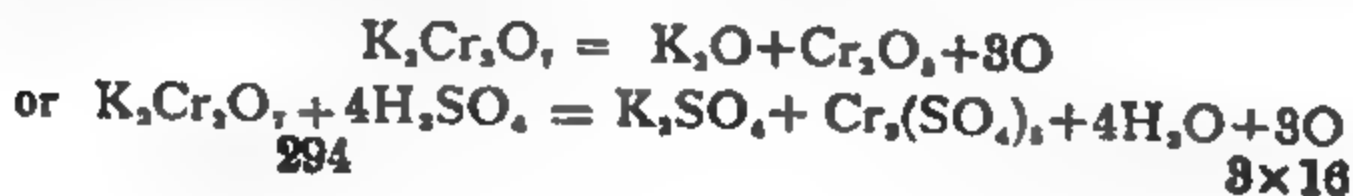


In practice sulphuric acid is always added to prevent the precipitation of the manganese as oxide, so that the equation becomes:—



Thus we see that $2 \times 158 = 316$ parts by weight of potassium permanganate supply $5 \times 16 = 80$ parts by weight (or 10 equivalents) of oxygen available for oxidation. Now, by definition, a normal solution of an oxidising agent is one that contains an equivalent weight (8 parts) of available oxygen per litre; hence the equivalent weight of potassium permanganate $= 316 \div 10 = 31.6$ gm., or one-fifth of its molecular weight, and a normal solution would contain 31.6 gm. per litre.

Another oxidising agent in common use is potassium dichromate. Its equivalent weight can be determined by similar considerations.



Each molecule of potassium dichromate (294) produces three atoms (or six equivalents) of oxygen for oxidation. Hence its equivalent will be one-sixth of its molecular weight. A normal solution of potassium dichromate will therefore contain 49 gm. of the salt per litre.

In the case of potassium dichromate, as well as of potassium permanganate, approximately decinormal solutions are generally used.

Once the solution of the oxidising agent has been made up and standardised (its normality determined) it may be regarded for simplicity as a solution of oxygen of the same normality, and need only appear as such in equations representing its oxidation actions.

Potassium permanganate solution acts as its own indicator since it is a purple solution, while its products are colourless substances. With potassium dichromate, either potassium ferricyanide is used as an external indicator or diphenylamine as an internal indicator.

Example 1. A solution of potassium permanganate was standardised by titrating it against weighed amounts of sodium oxalate in the presence of sulphuric acid. 0.237 gm. of sodium oxalate require 40.15 c.c. of permanganate. Calculate the normality of the solution.

(The method of calculation will be the same as that under I, page 117.)

As there is sulphuric acid present in solution, the sodium oxalate will be converted to oxalic acid and its equivalent weight like that of oxalic acid (see above) will be one-half of its molecular weight = 67.

By definition, an equivalent weight of sodium oxalate will be oxidised by 10000 c.c. $N/10$ potassium permanganate.

or 67 gm. $(\text{COONa})_2 \equiv 10000$ c.c. of $N/10$ KMnO_4

$\therefore 0.237$ „ „ $\equiv 10000 \times \frac{0.237}{67}$ c.c. of $N/10$ KMnO_4

but 0.237 „ „ $\equiv 40.15$ c.c. of $xN/10$ KMnO_4

This means that 40.15 c.c. of $xN/10$ solution $\equiv 10000 \times \frac{0.237}{67}$ c.c. of $N/10$ solution

$$\therefore x = \frac{10000}{40.15} \times \frac{0.237}{67} = 0.881$$

\therefore solution is 0.881 $N/10$.

Example 2. 20 c.c. of a solution of hydrogen peroxide were diluted to 500 c.c. and 25 c.c. portions of this dilute solution titrated against .97 *N*/10 potassium permanganate solution, 18.05 c.c. being required. Find the concentration of the hydrogen peroxide and its "volume strength."

Although hydrogen peroxide is itself an oxidising agent it reacts with potassium permanganate to form water and free oxygen.



This means that one gram molecule of H_2O_2 is oxidised by 16 gm. of oxygen or 2 litres of *N* KMnO_4 .

Hence the equivalent weight will be half the molecular weight

$$= \frac{34}{2} = 17$$

Calculation of the Concentration of the H_2O_2 Solution

$$25.00 \text{ c.c. of } \text{H}_2\text{O}_2 \equiv 18.05 \text{ c.c. of } .97 \text{ } N/10 \text{ } \text{KMnO}_4$$

$$\therefore \text{normality of the diluted solution} = \frac{18.05}{25.00} \times .97 \text{ } N/10$$

$$\text{and it contains } \frac{18.05}{25} \times .97 \times \frac{17}{10} \text{ gm. per litre}$$

But 1,000 c.c. of the dilute solution contained the same amount of H_2O_2 as 40 c.c. of the original solution which would thus contain,

$$\begin{aligned} & \frac{18.05}{25} \times .97 \times \frac{17}{10} \times \frac{1000}{40} \text{ gm. litre} \\ & = 29.77 \text{ gm. per litre.} \end{aligned}$$

Calculation of Volume Strength

The "volume strength" of hydrogen peroxide is defined as the number of times its own volume of oxygen a sample of hydrogen peroxide solution will evolve if decomposed naturally.



Now in the oxidation of H_2O_2 by permanganate, the oxygen evolved comes equally from the H_2O_2 and the permanganate; but 1 litre of *N* $\text{KMnO}_4 \equiv 8$ gm. of oxygen or 5.6025 litres (the equivalent volume)

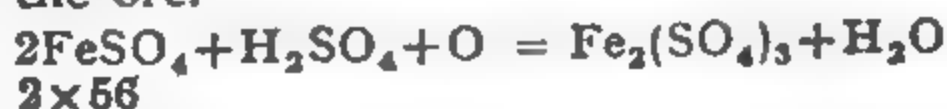
$\therefore 18.05 \text{ c.c. of } .97 \text{ } N/10 \text{ } \text{KMnO}_4 \equiv 5602.5 \times \frac{18.05}{1000} \times \frac{97}{10} \text{ c.c. of oxygen} = 9.81 \text{ c.c.}$, and this is also the volume of oxygen given off by 25 c.c. of the diluted H_2O_2 solution which contains 1 c.c. of the original solution and hence 9.81 is the "volume strength" of the peroxide.

The volume strength may also be calculated directly from the concentration

$$\begin{array}{rcl} 2\text{H}_2\text{O}_2 & = & 2\text{H}_2\text{O} + \text{O}_2 \\ 68 \text{ gm. H}_2\text{O}_2 & \text{evolve} & 22410 \text{ c.c. of oxygen} \\ \therefore 1 \text{ c.c. of the solution containing } .02977 \text{ gm. H}_2\text{O}_2 & \text{evolve} & \\ 22410 \times \frac{.02977}{68} \text{ c.c.} & & = 9.81 \text{ c.c.} \end{array}$$

The first method is advised where only the "volume strength" and not the concentration is required.

Example 3. 0.478 gm. of an iron ore were dissolved in dilute acid and titrated with .989 N/10 potassium dichromate solution, 7.55 c.c. being required. After reduction of the whole solution with stannous chloride, 29.70 c.c. of dichromate were required. Calculate the percentages of ferrous and of ferric iron in the ore.



During the first titration only the iron present in the ferrous state will be oxidised and is hence equivalent to 7.55 c.c. of .989 N/10 $\text{K}_2\text{Cr}_2\text{O}_7$.

After reduction with stannous chloride all the iron will be in the ferrous state and so the titration, 29.70 c.c. of .989 N/10 $\text{K}_2\text{Cr}_2\text{O}_7$ is equivalent to the total iron present.

By subtraction the ferric iron $\equiv 29.70 - 7.55 = 22.15$ c.c. of .989 N/10 $\text{K}_2\text{Cr}_2\text{O}_7$.

Ferrous Iron

The ferrous iron is oxidised by 7.55 c.c. of .989 N/10 $\text{K}_2\text{Cr}_2\text{O}_7$.

\therefore it contains $\frac{7.55}{1000} \times \frac{.989}{10}$ equivalents of iron.

\therefore the weight of Fe is $= \frac{7.55}{1000} \times .989 \times \frac{56}{10}$

\therefore percentage of ferrous iron $= 7.55 \times .989 \times \frac{.56}{10} \times \frac{100}{0.478}$
 $= 8.79\%$

Ferric Iron

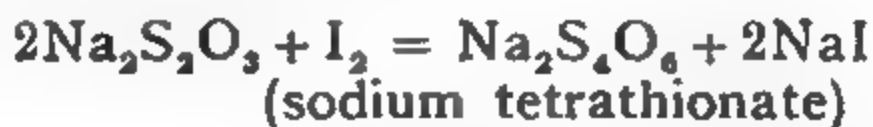
By similar reasoning the percentage of ferric iron may be

shown to be $= \frac{22.15}{1000} \times .989 \times \frac{56}{10} \times \frac{100}{0.478} = 25.78\%$.

(It should be realised that this calculation is merely a variation of method III, page 118. In this case, as the iron is not made up to a definite volume, we calculate the number of equivalents that it contains rather than its normality.)

IODINE TITRATIONS

The usefulness of iodine in volumetric analysis is chiefly due to its reaction with sodium thiosulphate which provides a satisfactory method of measuring the iodine liberated by a reaction:—

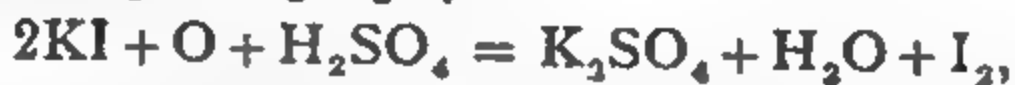


All titrations are carried out in a solution of potassium iodide which is a solvent for iodine and prevents it from being precipitated. Iodine, even in small traces, gives an intense blue colour to starch solution; so when the titration is nearing completion and the yellow colour due to the iodine is becoming faint, a few drops of starch solution are added and the titration continued until the dark blue coloration just disappears.

The equivalent weight of iodine is the same as its atomic weight, since iodine is a univalent element. From the equation above it will be seen that one gram molecular weight of thiosulphate reacts with one equivalent of iodine and hence the gram molecular weight of sodium thiosulphate is also its equivalent weight.

STANDARDISATION OF SODIUM THIOSULPHATE SOLUTION

Sodium thiosulphate may be standardised against a weighed amount of pure, resublimed iodine, but other methods are more convenient. Generally an approximately decinormal solution of sodium thiosulphate is made up by weighing out one-tenth of its gram molecular weight and making it up to one litre of solution. Iodine is now liberated from excess potassium iodide solution by adding a given volume of an oxidising agent, *e.g.*, 25 c.c. of KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$.



the iodine formed being equivalent to the amount of oxidising agent added. Thus 25 c.c. $N/10$ KMnO_4 solution added to an excess of potassium iodide solution will produce 25 c.c. $N/10$ iodine solution. This iodine is now titrated by running in the solution of sodium

thiosulphate to be standardised and the normality of the thiosulphate calculated.

Example. 25 c.c. of a 1.14 N/10 solution of potassium dichromate were added to an excess of potassium iodide solution and titrated with sodium thiosulphate solution, 25.95 c.c. being required. Calculate the normality of the thiosulphate solution.

25 c.c. of 1.14 N/10 $K_2Cr_2O_7 \equiv 25 \times 1.14$ c.c. of N/10 iodine solution,

and 25.95 c.c. of thiosulphate solution $\equiv 25 \times 1.14$ c.c. N/10 iodine

\therefore normality of thiosulphate solution is $\frac{25.00}{25.95} \times 1.14$ N/10
 $= 1.098$ N/10

The applications of the iodine titration are somewhat numerous and only a few examples can be given here.

Example 1. 25 c.c. of chlorine water were added to an excess of potassium iodide solution and the liberated iodine titrated with .97 N/10 sodium thiosulphate solution, 28.50 c.c. being required. Calculate the concentration of chlorine in gm. per litre.



The iodine liberated will be equivalent to the chlorine present. Hence 1 litre of N/10 Cl_2 solution \equiv 1 litre of N/10 I_2 solution \equiv 1 litre of N/10 $Na_2S_2O_3$ solution.

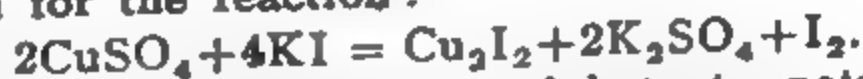
25 c.c. of chlorine solution = 28.50 c.c. of .97 N iodine solution.

Normality of the chlorine water = $\frac{28.50}{25.00} \times .97$ N/10.

Concentration = $\frac{28.50}{25.00} \times .97 \times \frac{35.46}{10}$ gm. per litre.
 $= 3.921$ gm. per litre.

Example 2. 3.143 gm. of a copper ore were dissolved in acid and made up to 500 c.c. 50 c.c. of this solution were added to an excess of potassium iodide solution. 26.75 c.c. of 1.21 N/10 sodium thiosulphate solution were required to titrate the liberated iodine. Calculate the percentage of copper in the ore.

Equation for the reaction:—



On addition of copper (cupric) sulphate to potassium iodide solution, cuprous iodide is precipitated and an equivalent amount of iodine liberated. Each molecule of copper salt (or

each atom of copper) liberates one atom (one equivalent) of iodine. The equivalent weight of copper in the reaction is thus the same as its atomic weight 63.57.

Now, 50 c.c. of CuSO_4 solution \equiv iodine solution \equiv 26.75 c.c. of 1.21 $N/10$ thiosulphate solution.

\therefore normality of CuSO_4 solution is $\frac{26.75}{50.00} \times 1.21 \text{ } N/10$

and concentration is $\frac{26.75}{50} \times 1.21 \times \frac{63.57}{10}$ gm. litre

\therefore percentage of copper in the ore $= \frac{26.75}{50} \times 1.21 \times \frac{63.57}{10} \times \frac{100}{3.143 \times 2}$
 $= 65.4\%$

Example 3. 1.278 gm. of commercial arsenious oxide were dissolved in a dilute solution of sodium bicarbonate, made up to 250 c.c. and titrated against 25 c.c. portions of a .99 $N/10$ solution of iodine, 25.19 c.c. being the average result of a titration. Calculate the percentage purity of the oxide.



198 = 4 equivalents.

The sodium bicarbonate is added to remove the hydroiodic acid as quickly as it is formed and hence to ensure the completion of the reaction from left to right.

4 equivalents of iodine react with one molecular weight of As_2O_3 , hence the equivalent weight of As_2O_3 is one quarter of its molecular weight $= \frac{198}{4} = 49.5$.

25.19 c.c. of As_2O_3 solution \equiv 25.00 c.c. of .99 $N/10$ iodine

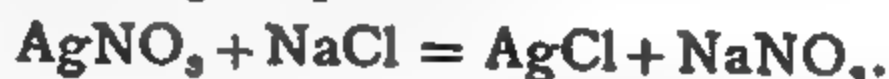
\therefore the normality of the As_2O_3 solution $= \frac{25.00}{25.19} \times .99 \text{ } N/10$.

\therefore concentration $= \frac{25.00}{25.19} \times .99 \times \frac{49.5}{10}$ gm. per litre

\therefore percentage of $\text{As}_2\text{O}_3 = \frac{25.00}{25.19} \times .99 \times \frac{49.5}{10} \times \frac{100}{1.278 \times 4}$
 $= 95.15\%$

PRECIPITATION ANALYSIS

When silver nitrate solution reacts with a chloride, silver chloride is precipitated.



This reaction is applied to the determination of chlorides,

a decinormal solution of silver nitrate being used. A definite volume of the chloride solution is taken and silver nitrate run in from a burette. A few drops of potassium chromate solution are added as indicator. Each addition of silver nitrate from the burette causes a precipitation of white silver chloride, but not of silver chromate, which is less insoluble. As soon as all the chloride has been precipitated, however, the next drop of silver solution will produce a precipitate of dark red silver chromate. The appearance of a slight, permanent, reddish brown coloration indicates the end point of the reaction. As silver chromate is soluble in dilute acids and in ammonium hydroxide solution, the titration must be carried out in neutral solution.

From the equation above it will be seen that one molecule of silver nitrate precipitates one equivalent of chloride and hence the equivalent weight of silver nitrate is the same as its molecular weight. A normal solution of silver nitrate therefore contains a gram molecular weight $(108 + 14 + 48) = 170$ gm. per litre.

Silver nitrate solution is most conveniently standardised by accurately weighing out some pure potassium chloride, making it up to a definite volume and titrating 25 c.c. samples of this solution with the silver nitrate solution.

Example 1. In order to standardise an approximately decinormal solution of silver nitrate, 1.472 gm. of potassium chloride were weighed out and dissolved in distilled water so as to make 250 c.c. of solution. A 25 c.c. sample of this solution required on the average 21.13 c.c. of silver nitrate solution for titration. Calculate the normality of the silver nitrate solution.

The equivalent of potassium chloride is $39.1 + 35.46 = 74.56$.

A decinormal solution \therefore contains 7.456 gm. per litre and so a

solution containing 1.472 gm. in 250 c.c. is $\frac{4 \times 1.472}{7.456} N/10$

Now 21.13 c.c. of silver nitrate solution \equiv 25 c.c. of $\frac{4 \times 1.472}{7.456} N/10$
 $N/10$ KCl.

\therefore normality of silver nitrate is $\frac{25.00}{21.13} \times \frac{4 \times 1.472}{7.456} N/10$
 $= .934 N/10$

Example 2. 250 c.c. of a natural water required 21.8 c.c. of .934 *N*/100 silver nitrate solution for titration. Calculate the chlorine content of the water expressed as grams of chlorine per 100 litres of water.

250 c.c. of water \equiv 21.8 c.c. of .934 *N*/100 silver nitrate solution, hence the normality of the water with respect to chlorine is :—

$$\frac{21.8}{250} \times .934 \text{ } N/100.$$

The equivalent of chlorine is 35.46,

and so the concentration of the solution is $\frac{21.8}{250} \times .934 \times \frac{35.46}{100}$ gm. Cl_2 .

\therefore weight in 100 litres would be $\frac{21.8}{250} \times .934 \times \frac{35.46}{100} \times 100 = 2.892$ gm.

VOLHARD'S METHOD FOR THE ESTIMATION OF SILVER

Silver nitrate reacts with ammonium thiocyanate according to the following equation :—



If a small quantity of ferric indicator (iron alum and nitric acid) is placed in the silver solution, completion of the reaction will be shown by the appearance of a permanent pink colour due to ferric thiocyanate which is produced by even the minutest excess of thiocyanate after the silver has all been precipitated. This is a much more sensitive end point than that given by silver chromate in the direct silver nitrate-chloride titration, and so the reaction has given rise to an important volumetric method for the estimation of silver or of chlorides. It has the additional advantages that the titration may be carried out in acid solution, also that it is not disturbed by the presence of considerable amounts of copper and other metallic impurities in the silver.

In order to estimate a chloride, a known weight of the solid material is dissolved in water and an accurately measured volume of standard silver nitrate solution, in slight excess of that required to precipitate all the chloride, is added. The solution is next boiled to coagulate the silver chloride, filtered and the excess of silver

nitrate estimated by titration with standard ammonium thiocyanate solution.

Example. 0.192 gm. of a solid chloride were dissolved in water and the chlorine precipitated by the addition of 50 c.c. of 1.017 *N*/10 silver nitrate solution. After filtering off the silver chloride the excess silver nitrate was titrated by running in 0.98 *N*/10 ammonium thiocyanate solution, 18.40 c.c. being required. Calculate the percentage of chlorine in the chloride.

(This calculation is similar to method IV on page 119.)

50 c.c. of 1.017 *N*/10 silver nitrate solution $\equiv 50 \times 1.017$ c.c. of *N*/10 solution.

$$= 50.85 \text{ c.c.}$$

and 18.40 c.c. of 0.98 *N*/10 NH_4CNS solution $\equiv 18.40 \times .98$ c.c. of *N*/10 solution

$$= 18.05 \text{ c.c.}$$

The chloride present will be equivalent to the silver nitrate used, which is the difference of these two volumes of decinormal solution.

$$= 50.85 \text{ c.c.} - 18.05 \text{ c.c.} = 32.80 \text{ c.c. of } N/10 \text{ solution.}$$

\therefore it contains $\frac{32.80}{1000} \times \frac{1}{10}$ equivalents of chloride.

The equivalent weight of chlorine is 35.46 gm.

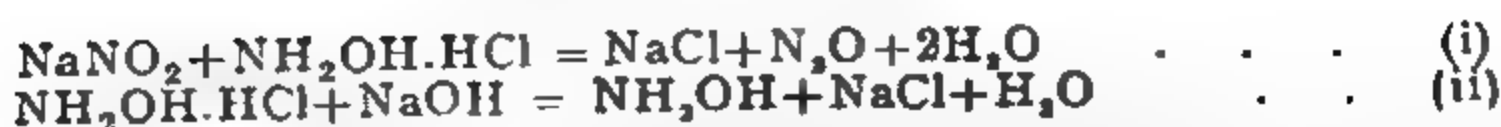
$$\therefore \text{the weight of chlorine} = \frac{32.80}{1000} \times \frac{35.46}{10} \text{ gm.}$$

$$\begin{aligned} \text{and percentage} &= \frac{32.80}{1000} \times \frac{35.46}{10} \times \frac{100}{0.192} \\ &= 60.57\% \end{aligned}$$

MISCELLANEOUS CALCULATIONS ON VOLUMETRIC ANALYSIS

Four more examples now follow to illustrate how the principles used in the calculations above are applied in connection with the results of analyses which employ other standard solutions and in the working of specific problems.

Example 1. 4.78 gm. of sodium nitrite were weighed out and made up to a litre with distilled water. 25 c.c. samples were taken and each heated with 25 c.c. of a 1.01 *N*/10 solution of hydroxylamine hydrochloride. After cooling, the excess hydroxylamine was estimated by titration with .96 *N*/10 caustic soda solution, an average of 9.60 c.c. being required. Calculate the percentage purity of the sample.



From equation (i) it is seen that one molecule of sodium nitrite is equivalent to one molecule of hydroxylamine and from equation (ii) that one molecule of hydroxylamine is equivalent to one of caustic soda.

$$\begin{aligned} \text{Volume of hydroxylamine hydrochloride} \\ = 25.00 \times 1.01 \text{ } N/10 = 25.25 \text{ c.c. } N/10 \end{aligned}$$

$$\begin{aligned} \text{Volume of sodium hydroxide required} \\ = 9.60 \times 0.98 \text{ } N/10 = 9.20 \text{ c.c. } N/10 \end{aligned}$$

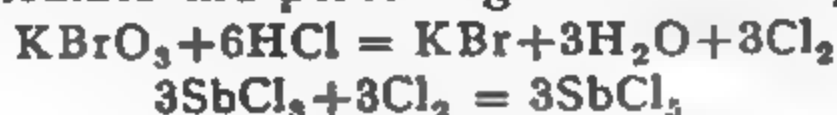
$$\therefore \text{Volume of } \text{NH}_2\text{OH} \cdot \text{HCl} \equiv 25 \text{ c.c.} \quad \text{NaNO}_2 = \underline{16.05 \text{ c.c. } N/10}$$

$$\text{and so normality of sodium nitrite solution} = \frac{16.05}{25.00} \times N/10$$

$$\text{and its concentration} = \frac{16.05}{25.00} \times \frac{69}{10} \text{ gm. per litre}$$

$$\begin{aligned} \therefore \text{percentage purity of sodium nitrite} &= \frac{16.05}{25.00} \times \frac{69 \times 100}{10} \quad 4.78 \\ &= 92.66\% \end{aligned}$$

Example 2. 0.102 gm. of an antimony ore were dissolved in acid and reduced to the tervalent state by means of SO_2 . After boiling off the excess SO_2 , the solution was titrated with a .98 $N/10$ solution of potassium bromate, the end point being indicated by the presence of methyl orange, whose colour fades when excess bromate is present. 14.63 c.c. of bromate were required. Calculate the percentage of antimony in the ore.



Potassium bromate is thus used as an oxidising agent to change the antimony from the tervalent to the pentavalent condition.

1 Mol. $\text{KBrO}_3 \equiv 3$ Mols. Cl_2 , which oxidise 3 Mols. SbCl_3 to SbCl_5

$$\begin{aligned} \therefore 1/6 \text{ Mol. } \text{KBrO}_3 &\equiv 1 \text{ equivalent } \text{Cl}_2 \equiv \frac{1}{2} \text{ Atomic wt. of Sb.} \\ &= \frac{121.76}{2} = 60.88 \text{ gm.} \end{aligned}$$

The equivalent weight of antimony is thus 60.88.
0.102 gm. of Sb \equiv 14.63 c.c. of .98 $N/10$ solution.

$$\text{and } \therefore \text{contain } \frac{14.63}{1000} \times \frac{.98}{10} \text{ equivalents of antimony.}$$

The weight of Sb in the solution $\therefore = \frac{14.63}{1000} \times .98 \times \frac{60.88}{10}$ gm. per litre, and the percentage of antimony in the ore

$$\begin{aligned} &= \frac{14.63}{10000} \times .98 \times \frac{60.88}{10} \times 100 \\ &= 85.5\% \end{aligned}$$

Example 3. 0.746 gm. of a mixture of sodium and potassium chlorides was dissolved in water and made up to 250 c.c. A 50 c.c. portion of this solution required 25.6 c.c. of a .97 *N*/10 solution of silver nitrate for titration. Calculate the percentage of sodium chloride in the mixture.



50 c.c. of chloride solution \equiv 25.6 c.c. of .97 *N*/10 silver nitrate

$$\therefore \text{normality of the chloride solution} = \frac{25.60}{50.00} \times .97 \text{ } N/10$$

$$\text{and its concentration} = \frac{25.60}{50.00} \times .97 \times \frac{35.46}{10} \text{ gm. chlorine per litre}$$

$$\text{or } \frac{25.60}{50.00} \times .97 \times \frac{35.46}{10} \times \frac{1}{4} \text{ gm. per 250 c.c.}$$

$$= 0.4402 \text{ gm.}$$

This means that 0.746 gm. of the mixed chlorides contain 0.4402 gm. of chlorine.

Let x = the weight of NaCl in the mixture, then $0.746 - x$ = the weight of KCl.

$$x \text{ gm. of NaCl contain } x \times \frac{35.46}{58.46} \text{ gm. of chlorine}$$

$$\text{and } 0.746 - x \text{ gm. of KCl contain } (0.746 - x) \times \frac{35.46}{74.56} \text{ gm. of chlorine}$$

but the total weight of chlorine in the mixture is 0.4402 gm.

$$\therefore x \times \frac{35.46}{58.46} + (0.746 - x) \times \frac{35.46}{74.56} = 0.4402$$

$$\therefore x = 0.6525 \text{ gm. or } \frac{0.6525}{0.746} \times 100\% \text{ NaCl}$$

$$= 87.5\% \text{ NaCl in the mixture.}$$

Example 4. The chloride of a non-metallic element X when vaporised had a vapour density of 84.9 at a temperature at which there was no evidence of dissociation. 0.8592 gm. of the chloride were dissolved in water, complete hydrolysis taking place. The acid solution required 45.4 c.c. of .89 *N*/2 caustic soda solution for neutralisation. Calculate the atomic weight of the element.

The approximate molecular weight of the chloride = $2 \times$ its vapour density = $2 \times 84.9 = 169.8$



Thus for every atom of chlorine present in the molecular weight, one litre of normal HCl solution will be formed. The equivalent weight of the chloride will be that weight that contains

one equivalent of chlorine, that produces one equivalent of hydrochloric acid, and that requires one litre of N NaOH for neutralisation.

45.4 c.c. of .89 $N/2$ caustic soda solution \equiv 0.8592 gm. of the chloride

\therefore 1000 c.c. of N caustic soda solution $\equiv .8592 \times \frac{1000 \times 2}{45.4 \times .89}$ of the chloride = 42.52 c.c.

The accurate equivalent weight of the chloride is thus = 42.52.

But the approximate molecular weight of the compound is 169.8.

$$\therefore \text{valency of the element} = \frac{169.8}{42.52} = 4$$

The equivalent weight of the element = equivalent of the chloride—equivalent of chlorine = 42.52—35.46 = 7.06.

\therefore Accurate atomic weight of the element = 7.06 \times 4 = 28.24.

PROBLEMS ON VOLUMETRIC ANALYSIS

(The answers to problems with odd numbers will be found at the end of the book)

ACID-ALKALI TITRATIONS

- 291 Calculate the normality of solutions of nitric and sulphuric acids each containing 124.8 gm. per litre.
- 292 Calculate the concentration in grams per litre of a solution of acetic acid, the normality of which is the same as that of a solution of caustic potash containing 5.720 gm. per litre.
- 293 Calculate the concentration in grams per litre of a 2.35 N solution of (a) nitric acid
(b) oxalic acid
(c) barium hydroxide.
- 294 What is the concentration expressed in grams per litre of 0.127 N solutions of (a) H_2SO_4
(b) HNO_3
(c) acetic acid; and what indicators would you use in titrating them with NaOH solution?
- 295 A solution of barium hydroxide is known to contain 0.00816 gm. per c.c. Calculate its normality; also what would be the concentration of a solution of caustic soda of the same normality?
- 296 20 c.c. of a solution of sulphuric acid required for neutralisation 25.2 c.c. of a solution of caustic soda of normality .92 $N/10$. Calculate the normality and concentration of the acid.

- 297 An approximately decinormal solution of sulphuric acid was standardised by titration against weighed quantities of anhydrous sodium carbonate. It was found that 0.20 gm. of carbonate were neutralised by 39.20 c.c. of sulphuric acid. Calculate the normality of the acid.
- 298 20 c.c. of ammonia of specific gravity 0.940 were dissolved in distilled water and made up to 250 c.c. 25 c.c. portions required, on an average, 19.8 c.c. of .875 *N* HCl for neutralisation. Calculate the percentage of ammonia in the solution.
- 299 19.6 c.c. of H_2SO_4 density 1.674 were mixed with water and the volume made up to 1 litre. 25 c.c. of the solution required 25.20 c.c. .973 *N/2* NaOH for neutralisation. Find the % of pure H_2SO_4 .
- 300 25 c.c. of a solution containing a mixture of formic, acetic and oxalic acids was diluted to one litre and 25 c.c. samples titrated against .86 *N/10* caustic soda solution, an average volume of 18.2 c.c. being required. Calculate the acidity of the original solution as expressed by the concentration of replaceable hydrogen per litre.
- 301 How much .935 *N* alkali would be required to neutralise the acid produced by the complete hydrolysis of .5 gm. of sulphuryl chloride?
- 302 3.85 gm. of impure tartaric acid were dissolved in water and made up to 250 c.c. 25 c.c. portions of the diluted solution were titrated against a .97 *N/10* caustic soda solution, using phenolphthalein as indicator, 18.93 c.c. being the average titration result. Calculate the percentage purity of the acid.
- 303 How much .935 *N* alkali would be required to neutralise the acid produced by the hydrolysis of .5 gm. PCl_5 , using litmus as indicator?
- 304 0.4 gm. of phosphorus was burnt to the oxide and dissolved in excess boiling water. The solution was titrated with *N/10* NaOH, using litmus as indicator. How much was required?
- 305 What volume of .981 *N/2* HCl is required to neutralise .6732 gm. of Na_2CO_3 , when (a) methyl orange is used as indicator and (b) when phenolphthalein is used?
- 306 2.510 gm. of ferrous ammonium sulphate were heated with excess caustic soda and the ammonia evolved passed into 50 c.c. of 1.13 *N/2* sulphuric acid. The excess acid required 17.78 c.c. of .89 *N* caustic soda solution for neutralisation. Calculate the percentage of ammonia in the salt.
- 307 5 gm. of ammonium chloride were heated with 5 gm. of calcium oxide and the resulting gas led into excess of *N/10* hydrochloric acid solution. What volume of this solution would be neutralised?

- 308 0.664 gm. of an ammonium salt was decomposed by heating with caustic soda solution and the liberated ammonia absorbed in 50 c.c. of .9 *N* sulphuric acid. The excess acid, after absorption, required 29.9 c.c. 1.1 *N* caustic soda solution. Calculate the percentage of ammonia in the salt.
- 309 1.437 gm. of an ammonium compound were heated with NaOH and the ammonia evolved passed into 25 c.c. of .640 *N* H_2SO_4 . After the ammonia evolution had ceased the excess acid was titrated with .1079 *N* NaOH and 80.29 c.c. were required. Find the percentage of ammonia in the compound.
- 310 1.263 gm. of an organic nitrogen compound were reduced to ammonium salts by Kjeldahl's method. On addition of excess caustic soda and heating, the ammonia was driven off and absorbed in 50 c.c. of 1.31 *N*/2 sulphuric acid, 34.9 c.c. of 1.29 *N*/2 caustic soda being required to neutralise the excess acid. Calculate the percentage of nitrogen in the compound.
- 311 25 c.c. of a solution of calcium sulphate was boiled with 50 c.c. of 1.2 *N*/10 sodium carbonate, filtered and the excess carbonate found by titration with .99 *N*/10 sulphuric acid, 26.2 c.c. being required. What was the concentration of the calcium sulphate solution?
- 312 The temporary hardness of a sample of water was determined by titration with standard acid, 100 c.c. of water requiring 9.6 c.c. of .97 *N*/20 acid for neutralisation. Calculate the temporary hardness of the water expressed as gm. of CaCO_3 per 100,000 gm. of water.
- 313 100 c.c. of a sample of water was titrated with 1.21 *N*/20 sulphuric acid for the determination of its temporary hardness. 7.9 c.c. were required. In determining the permanent hardness 25 c.c. of 1.24 *N*/20 sodium carbonate solution was added to a further 100 c.c., the solution boiled, filtered and titrated with the same standard acid, 19.6 c.c. being required. Calculate the temporary and the permanent hardness of the water expressed as parts of CaCO_3 and CaSO_4 respectively, in 100,000 parts of water.
- 314 What volume *N*/2 acid is required to neutralise a mixture of .4 gm. KOH and .5 gm. K_2CO_3 with phenolphthalein as indicator?
- 315 A mixture of .5 gm. each of NaOH, Na_2CO_3 and NaHCO_3 is dissolved in water and titrated with *N* H_2SO_4 . What volume is required, using (a) phenolphthalein and (b) methyl orange?
- 316 A solution of *N* NaOH is left exposed to CO_2 . It is found that 50 c.c. required 39.3 c.c. of .975 *N* acid for titration, using phenolphthalein as indicator. Calculate the volume of CO_2 absorbed at N.T.P.

- 317 What volume of $\cdot981$ $N/10$ H_2SO_4 is required to neutralise a mixture of $\cdot121$ gm. KOH and $\cdot161$ gm. K_2CO_3 , using (1) phenolphthalein, (2) methyl orange as indicators?
- 318 A solution is known to contain $0\cdot47$ gm. of anhydrous sodium carbonate, $1\cdot06$ gm. of sodium bicarbonate and $0\cdot03$ gm. of sodium hydroxide. Calculate the volume of $1\cdot22$ $N/2$ sulphuric acid which will be required to neutralise the solution, using as indicator (a) methyl orange and (b) phenolphthalein.
- 319 A solution was made by dissolving $12\cdot82$ gm. of a mixture of normal K_2SO_4 and acid $KHSO_4$ in half a litre of water. 25 c.c. of the solution were found to require $27\cdot8$ c.c. standard KOH (1 c.c. = $\cdot0055$ gm. KOH). Calculate the weight of each salt in 10 gm. of the mixture.
- 320 25 c.c. of a solution of a mixture of $NaOH$ and Na_2CO_3 require for neutralisation $10\cdot5$ c.c. $N/2$ H_2SO_4 with phenolphthalein as indicator and $15\cdot6$ c.c. with methyl orange. Calculate the weights of $NaOH$ and Na_2CO_3 in a litre of solution.
- 321 $\cdot46$ gm. of the oxide of a metal M required for neutralisation 60 c.c. $N/10$ HCl . The carbonate had the formula MCO_3 . What is the atomic weight of the metal?
- 322 $0\cdot3142$ gm. of an organic acid were dissolved in 25 c.c. of $1\cdot13$ $N/2$ caustic soda solution. The residual alkali required $15\cdot00$ c.c. of $\cdot99$ $N/2$ sulphuric acid for neutralisation. The acid gave a value of $22\cdot8$ in a vapour density determination. Calculate the equivalent weight and the basicity of the acid.
- 323 $0\cdot2573$ gm. of an organic acid are dissolved in 25 c.c. $1\cdot056$ $N/10$ $NaOH$ solution. It is found that $5\cdot2$ c.c. of $\cdot976$ $N/10$ H_2SO_4 are required to neutralise the excess of alkali. Find the gm. equivalent weight of the organic acid.
- 324 $0\cdot1123$ gm. of pure indium oxide were dissolved in 50 c.c. of $1\cdot11$ $N/10$ HCl and the excess acid titrated with $\cdot96$ $N/10$ $NaOH$ solution, $32\cdot55$ c.c. being required. A small quantity of the chloride extracted from the solution gave a value of 112 in a vapour density determination. Calculate the atomic weight of indium.
- 325 $0\cdot5691$ gm. of aluminium foil were dissolved in 100 c.c. of $\cdot96$ N hydrochloric acid and the excess acid determined by titration with $\cdot94$ N caustic soda solution, $35\cdot10$ c.c. being required. Calculate the equivalent weight of aluminium.

POTASSIUM PERMANGANATE AND POTASSIUM DICHROMATE

- 326 What weight of pure crystallised oxalic acid will be oxidised by $39\cdot8$ c.c. of $\cdot0960$ N potassium permanganate solution in the presence of excess dilute sulphuric acid.

- 327 0.5 gm. of a substance containing 35% iron, required for oxidation 40 c.c. KMnO_4 . How much ferrous ammonium sulphate would 1 c.c. of this solution oxidise? Calculate also the concentration of the KMnO_4 solution in gm. per litre.
- 328 10 c.c. of potassium permanganate in acid solution are decolorised by 0.56 gm. of ferrous ammonium sulphate. What volume of permanganate must be diluted to 1 litre with water to make the solution exactly $N/10$?
- 329 24.2 c.c. of a solution of oxalic acid were required to neutralise 25 c.c. of NaOH solution. 25 c.c. of the oxalic acid solution decolorised 36.3 c.c. of a KMnO_4 solution, 50 c.c. of a solution of ferrous ammonium sulphate required 23.1 c.c. of KMnO_4 solution or 34.65 of a $.25\ N/10$ solution of $\text{K}_2\text{Cr}_2\text{O}_7$ for complete oxidation. Determine the normality of the NaOH solution.
- 330 10 c.c. of a solution of ferrous sulphate require 10.3 c.c. of $0.101\ N\ \text{KMnO}_4$ for oxidation. How much Fe_2O_3 could be obtained from 60 c.c. of the ferrous sulphate solution?
- 331 0.5 gm. of an iron ore were dissolved in dilute H_2SO_4 and titrated with $N/10\ \text{KMnO}_4$, of which 6.25 c.c. were required. The whole was then reduced with a ZnCu couple, the acid again titrated, 31.25 c.c. being required. Find the percentage of ferrous and ferric iron in the ore.
- 332 1.211 gm. of a substance containing 21% iron require 30.1 c.c. of potassium permanganate solution for oxidation. Calculate the normality of the permanganate.
- 333 0.2240 gm. of pure iron were dissolved in pure H_2SO_4 and required for oxidation 43.2 c.c. of KMnO_4 solution. Calculate the normality of the KMnO_4 and its strength in terms of iron per c.c. of solution.
- 334 0.5 gm. of ferrous ammonium sulphate,
 $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$,
require 14.5 c.c. of KMnO_4 solution for oxidation. Calculate the strength of the KMnO_4 solution in terms of
(a) iron
(b) normality
(c) oxalic acid.
- 335 .3265 gm. of potassium persulphate was mixed with 25 c.c. of FeSO_4 acidified and well shaken. The excess of FeSO_4 was determined by titration with $.1023\ N\ \text{KMnO}_4$, 7.44 c.c. being required. If 25 c.c. FeSO_4 solution were equivalent to 30.58 c.c. of this KMnO_4 , calculate the percentage purity of the persulphate.

- 336 20 c.c. of a solution of oxalic acid require 21.1 c.c. of $N/10$ potassium permanganate for oxidation. How much calcium oxalate would 25 c.c. of the oxalic acid yield on treatment with calcium chloride?
- 337 0.314 gm. of the mixed oxalates of Na and K require for oxidation 58 c.c. $\cdot 77$ $N/10$ KMnO_4 . What is the percentage of sodium oxalate in the mixture?
- 338 1.4370 gm. of sodium nitrite were dissolved in water and made up to a volume of 250 c.c. 25 c.c. samples were quickly titrated with 1.023 $N/10$ potassium permanganate, 39.94 c.c. being required. Calculate the percentage purity of the nitrite.
- 339 0.207 gm. of pyrolusite was carefully weighed into a flask containing 25 c.c. of acidified standard ferrous sulphate solution in an inert atmosphere. After heating and completion of the reaction, the excess ferrous sulphate was determined by titration with 1.023 $N/10$ potassium permanganate solution, 7.57 c.c. being required. 25 c.c. of the ferrous sulphate solution were equivalent to 48.15 of the same permanganate solution. Calculate the percentage of MnO_2 in the pyrolusite.
- 340 1.1586 gm. of pig iron were dissolved in acid and the manganese present oxidised to permanganate by means of sodium bismuthate. 50 c.c. of ferrous sulphate were added and, after reaction, the excess determined by titration with $\cdot 425$ $N/10$ potassium permanganate solution, 3.04 c.c. being required. 50 c.c. of the ferrous sulphate solution were found to be equivalent to 35.90 c.c. of the same permanganate solution. Calculate the percentage of manganese in the iron.
- 341 10 c.c. H_2O_2 solution were diluted to 250 c.c. in a flask and 25 c.c. of this solution titrated against KMnO_4 , 33 c.c. being required. If the KMnO_4 is the same strength as a solution of $\text{K}_2\text{Cr}_2\text{O}_7$, 25 c.c. of which oxidised 0.16 gm. of pure iron find the volume strength of the H_2O_2 .
- 342 2.5 c.c. of a solution of Merck's "perhydrol" (concentrated hydrogen peroxide) was diluted to 500 c.c. with distilled water and 25 c.c. samples of this solution titrated with 1.06 $N/10$ potassium permanganate, an average volume of 21.15 c.c. being required. Calculate the concentration and the volume strength of the perhydrol.
- 343 0.527 gm. of barium peroxide contaminated with the monoxide were dissolved in an excess of dilute sulphuric acid and titrated with 1.07 $N/10$ potassium permanganate solution, 18.75 c.c. being required. Calculate the percentage purity of the peroxide.

- 344 0.514 gm. of sodium peroxide were dissolved in water and the volume of the solution made up to 250 c.c. 50 c.c. samples were titrated with 1.023 *N*/10 potassium permanganate, 16.13 c.c. being required. Calculate the percentage purity of the peroxide.
- 345 Calculate the volume strength of a solution of hydrogen peroxide, 10 c.c. of which were diluted to 250 c.c. with distilled water and 25 c.c. samples of the diluted solution titrated with 1.023 *N*/10 potassium permanganate solution, requiring 13.32 c.c.
- 346 4.12 gm. of anhydrous ferrous sulphate which had become partly oxidised was dissolved in 250 c.c. of water and the ferrous iron determined by direct titration of 25 c.c. samples with 1.07 *N*/10 potassium dichromate solution, an average volume of 18.73 c.c. being required. Calculate the percentage of ferrous sulphate in the sample.
- 347 0.3182 gm. of an iron ore were dissolved in acid and the ferrous iron determined by titration with 1.015 *N*/10 potassium dichromate solution, 16.49 c.c. being required. The total iron was determined by weighting out a further 1.8259 gm. of the same ore, dissolving in acid, reducing, diluting to 250 c.c. and titrating 50 c.c. samples with the same standard dichromate solution. 19.70 c.c. were required. Calculate the percentage of ferrous and of ferric iron in the ore.
- 348 0.47 gm. of powdered zinc was placed in a flask with 50 c.c. of .98 *N*/2 potassium dichromate solution. Dilute acid was then added until the zinc dissolved, when the solution was made up to 250 c.c. 10 c.c. portions of 1.16 *N*/10 ferrous sulphate solution were titrated with this solution, an average volume of 16.3 c.c. being required. Calculate the percentage purity of the zinc.
- 349 A quantity of ferrous ammonium sulphate was weighed out and dissolved in a litre of distilled water. 50 c.c. of this solution were titrated against .0941 *N* KMnO_4 solution, 24.32 c.c. being required. A further 50 c.c. of the ferrous ammonium sulphate solution was titrated against $\text{K}_2\text{Cr}_2\text{O}_7$ solution using an external indicator, when 31.45 c.c. were required. Calculate the normality of the $\text{K}_2\text{Cr}_2\text{O}_7$ solution.
- 350 The chromium in 0.6515 gm. of a chromium mineral was oxidised to chromate and converted to dichromate. 75 c.c. of a standard ferrous sulphate solution were added and the excess ferrous sulphate determined by titration with 1.016 *N*/10 potassium dichromate, 4.21 c.c. being required. 25 c.c. of the ferrous sulphate solution were equivalent to 44.19 c.c. of the potassium dichromate. Calculate the percentage of Cr_2O_3 in the mineral.

IODINE TITRATIONS

- 351 0.195 gm. of pure MnO_2 was heated with an excess of concentrated HCl and the gas evolved passed into KI solution. How much 1.126 $N/10$ thiosulphate solution would be required to titrate the iodine liberated?
- 352 0.203 gm. of impure manganese dioxide was heated with hydrochloric acid and the chlorine evolved passed into a solution of potassium iodide. The iodine thus liberated required 21.5 of .97 $N/10$ sodium thiosulphate solution. What is the percentage purity of the manganese dioxide?
- 353 5.0321 gm. of a Cu ore were dissolved in acid and the solution made up to 250 c.c. To 25 c.c. after neutralisation, excess KI was added and the liberated iodine titrated with 1.035 $N/10$ $\text{Na}_2\text{S}_2\text{O}_3$, 24.46 c.c. being required. Find the percentage of copper in the ore.
- 354 10.38 gm. of crystallised potassium cupric sulphate were dissolved in water and the salt made up to 250 c.c. 50 c.c. of the solution were treated with an excess of potassium iodide and the liberated iodine titrated with a solution of sodium thiosulphate, 23.95 c.c. being required. The percentage of copper in the salt is 14.3. Calculate the normality of the thiosulphate.
- 355 25 c.c. of .98 $N/10$ $\text{K}_2\text{Cr}_2\text{O}_7$ were added to excess acidified KI and required 23.1 c.c. thiosulphate to titrate the liberated iodine. 1.591 gm. of a Cu ore were dissolved in acid and made up to 250 c.c. 50 c.c. of this solution, neutralised and added to KI solution, required 24.69 c.c. of the same thiosulphate to decolorise the iodine. Find the percentage of Cu in the ore.
- 356 10 c.c. of a mixture of copper sulphate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and sodium chloride were dissolved in water and treated with excess potassium iodide, the iodine liberated requiring 48 c.c. of 0.13 N thiosulphate. Calculate the percentage of each salt in the mixture.
- 357 0.3471 gm. of lead peroxide was heated with hydrochloric acid and the chlorine evolved passed into excess potassium iodide solution and the iodine liberated titrated with .9956 $N/10$ sodium thiosulphate solution, 19.80 c.c. being required. What was the percentage of lead peroxide in the sample?
- 358 0.32 gm. of a sample of bleaching powder were treated with sulphuric acid and the chlorine evolved led into a solution of potassium iodide. The liberated iodine was titrated with .982 $N/10$ thiosulphate and required 26.40 c.c. What was the percentage of available chlorine in the bleaching powder?
- 359 0.2143 gm. of a chlorate was weighted out and heated with excess potassium iodide and hydrochloric acid solution in a pressure bottle and afterwards made up to 250 c.c. and

titrated in 50 c.c. samples against .9956 *N*/10 sodium thiosulphate, 16.95 c.c. being required. In a blank titration in which approximately the same amounts of potassium iodide and hydrochloric acid were heated together 4.18 c.c. of thiosulphate was required for the whole of the iodine set free. Calculate the percentage of chlorate in the sample.

- 360 0.9099 gm. of arsenious oxide was dissolved in a small amount of caustic soda solution, neutralised, some sodium bicarbonate added, and made up to 250 c.c. This solution was now titrated against 25 c.c. samples of a .8598 *N*/10 iodine solution, 29.46 c.c. being required. What was the purity of the arsenious oxide?
- 361 7.2014 gm. of bleaching powder were dissolved in water and the solution made up to one litre. 50 c.c. portions were taken, an excess of potassium iodide added and the solution strongly acidified. The iodine set free required 29.80 c.c. of .9956 *N*/10 sodium thiosulphate solution. Calculate the percentage available chlorine in the bleaching powder.
- 362 0.3545 gm. of sodium sulphite crystals was weighed into 50 c.c. of standard iodine solution when the excess iodine required 7.30 c.c. of .9956 *N*/10 sodium thiosulphate solution for titration. 25 c.c. of the iodine solution were equivalent to 17.15 c.c. of the same thiosulphate. Calculate the percentage purity of the crystals.
- 363 What is the percentage of copper in an ore, 0.5918 gm. of which, when dissolved in acid and excess potassium iodide added, liberated sufficient iodine to react with 24.69 c.c. of .9956 *N*/10 sodium thiosulphate solution?
- 364 2.134 gm. of a soluble antimony compound were dissolved in water, made up to 250 c.c. and 25 c.c. portions determined by titration with 1.243 *N*/10 iodine solution, 23.4 c.c. being an average value for a titration. Calculate the percentage of antimony in the compound.
- 365 3.584 gm. of impure sodium sulphide were dissolved in water and the solution made up to 250 c.c. As a mean of three titrations it was found that after acidification 25 c.c. of this solution required 25.72 c.c. of .97 *N*/10 iodine solution. What is the percentage of sodium sulphide in the salt?

SILVER TITRATIONS

- 366 Calculate the percentage of pure sodium chloride in a sample of salt from the following data:—0.1843 gm. of salt dissolved in water required 26.6 c.c. of 1.17 *N*/10 silver nitrate solution to precipitate all the chloride.
- 367 Calculate the concentration of a solution of ammonium chloride, 50 c.c. of which required 37.6 c.c. of *N*/10 AgNO_3 for titration.

- 368 0.1625 gm. of a metallic chloride was dissolved in water and added to 50 c.c. of $N/10$ AgNO_3 solution. The excess silver nitrate was titrated with .95 $N/10$ ammonium thiocyanate, of which 21.05 c.c. were required. Calculate the equivalent weight of the metal.
- 869 250 c.c. of London tap water were analysed for chlorine by direct titration with .9783 $N/100$ silver nitrate solution. As a mean of several titrations it was found that 12.63 c.c. were required. Calculate the concentration of chlorine in tap water expressed as parts of chlorine per 100,000 parts of water.
- 870 50 c.c. of a solution containing sodium and potassium chlorides gave on evaporation, 0.1500 gm. of the mixed anhydrous chlorides. 50 c.c. of this same solution required 24.2 c.c. of 0.985 $N/10$ AgNO_3 solution to precipitate all the chlorine as silver chloride. Calculate the weight of NaCl and KCl per litre of solution.
- 371 An English silver coin (1915) weighing 1.1957 gm. was dissolved in acid and the solution made up to 250 c.c. 50 c.c. portions of this solution were found to require on the average 11.83 c.c. of .9376 $N/10$ ammonium thiocyanate solution for titration. Calculate the percentage of silver in the coin.
- 372 0.196 gm. of the chloride of a quadrivalent metal was taken and 30 c.c. of an $N/10$ silver nitrate solution required for the complete precipitation of the chloride. Calculate the molecular weight of the chloride.
- 373 A silver coin weighing 12.327 gm. was dissolved in HNO_3 and the solution evaporated to dryness. The residue was dissolved in H_2O and made up to a litre. 25 c.c. of this solution react with 23.5 c.c. of 1.023 $N/10$ NaCl solution. Calculate the percentage of silver in the coin.
- 374 25 c.c. of a solution of hydrogen chloride were added to 50 c.c. of 0.099 N -silver nitrate. After filtration, the excess of silver nitrate on titration required 21.7 c.c. of 0.105 N ammonium thiocyanate. A second quantity of 25 c.c. of the same hydrochloric acid was added to 0.1122 gm. of a metallic carbonate. The excess of acid required 3.85 c.c. of 0.11 N NaOH for neutralisation. Calculate the equivalent weight of the metal in the carbonate.
- 375 1.33 gm. of a mixture of sodium and potassium chlorides were dissolved in water and treated with AgNO_3 in excess. The precipitate weighed 2.87 gm. Find the weight of NaCl in the mixture.

MISCELLANEOUS

- 376 20 c.c. of a solution of sulphur dioxide required 28.65 c.c. of a 1.04 *N*/10 iodine solution for titration. Calculate the concentration of the sulphur dioxide in grams per litre of solution.
- 377 0.2214 gm. of the carbonate of a metal were dissolved in 50 c.c. of *N*/10 HCl and the excess acid titrated with .98 *N*/10 alkali, 20.4 c.c. being required. The sulphate of the metal is isomorphous with anhydrite (CaSO_4). What is the atomic weight of the metal?
- 378 0.4571 gm. of an alloy of aluminium and magnesium was dissolved in 50 c.c. of .97 *N* hydrochloric acid. The excess acid required 43.2 c.c. of a 1.13 *N*/10 caustic soda solution for titration. What is the composition of the alloy?
- 379 1.1797 gm. of mercuric oxide were dissolved in acid and made up to 250 c.c. with distilled water. 50 c.c. portions were titrated with .9376 *N*/10 ammonium thiocyanate solution, 22.94 c.c. being required. Calculate the percentage of mercury in the oxide.
- 380 0.191 gm. of the mixed oxalates of sodium and potassium require for oxidation 30 c.c. of .87 *N*/10 KMnO_4 . What is the percentage of the sodium salt in the mixture?
- 381 25 c.c. of a volatile acid of density 1.56 were neutralised by running in at a uniform rate of 2 c.c. per second (a) 22.47 c.c. of 10 *N* alkali and (b) 40.03 c.c. of 5 *N* alkali. Calculate (a) the equivalent weight of the acid and (b) the rate at which it is evaporating (assuming this to be constant).
- 382 0.1233 gm. of an antimony ore was reduced to the trivalent state and titrated with a solution of potassium bromate, 14.59 c.c. being required. The bromate solution was standardised by titration with pure metallic antimony, 0.1691 gm. of Sb requiring 27.61 c.c. Calculate the percentage of antimony in the ore.
- 383 0.2266 gm. of the chloride of a metal was dissolved in water and the chloride precipitated after acidification by the addition of 50 c.c. of .9783 *N*/10 silver nitrate solution. The precipitate was filtered off and the excess of silver nitrate determined by titration with .9376 *N*/10 ammonium thiocyanate solution, 10.88 c.c. being required. Calculate the percentage of chloride in the salt.
- 384 0.4716 gm. of a chromium containing mineral was oxidised with sodium peroxide and the resulting sodium chromate acidified and 50 c.c. of 0.1382 *N* ferrous ammonium sulphate solution added. The excess ferrous ammonium sulphate required 18.45 c.c. of 0.099 *N* potassium permanganate for oxidation. Calculate the percentage of chromium in the mineral.

- 385 0.8976 gm. of a tin ore was converted to an acid solution of stannic chloride and reduced with metallic antimony. The stannous chloride was now titrated with .3258 *N*/10 iodine solution, 55.66 c.c. being required. Calculate the percentage of tin in the ore.
- 386 0.68 gm. of calcium carbonate were dissolved in acid and the calcium precipitated by ammonium oxalate. The calcium oxalate was decomposed with dilute acid, the liberated oxalic acid made up to 250 c.c. and 25 c.c. portions titrated with .99 *N*/10 potassium permanganate solution, 11.7 c.c. being required. Calculate the percentage of purity of the carbonate.
- 387 4.5278 gm. of sodium nitrite were dissolved in water and the solution made up to one litre. 25 c.c. portions were mixed with 25 c.c. portions of a solution of hydroxylamine hydrochloride and the excess hydroxylamine determined by titration with 1.071 *N*/10 caustic soda solution, 32.27 c.c. being required. 25 c.c. of the hydroxylamine solution were equivalent to 47.54 c.c. of the same caustic soda solution. Calculate the percentage purity of the nitrite.
- 388 0.3090 gm. of potassium persulphate were dissolved in 25 c.c. of an acidified ferrous sulphate solution (1.21 *N*/10). After completion of the reaction the excess of FeSO_4 was determined by titration with 1.02 *N*/10 potassium permanganate, 8.69 c.c. being required. Calculate the percentage purity of the persulphate.
- 389 0.7632 gm. of a sample of linseed cake was heated with acid and metallic copper to reduce the organic nitrogen to ammonia. Excess caustic soda was added and the ammonia distilled into 25 c.c. of .5488 *N* sulphuric acid. After all the ammonia had been evolved 99.43 c.c. of 1.071 *N*/10 caustic soda were required to titrate the excess acid. Calculate the percentage of nitrogen in the linseed cake.
- 390 0.5746 gm of a zinc ore were dissolved in acid, metallic impurities removed and the solution titrated with a standard solution of potassium ferrocyanide (0.2456 gm. $\text{Zn} \equiv 24.55$ c.c. ferrocyanide) using uranyl nitrate as indicator, 26.45 c.c. being required. The equation for the reaction is:—

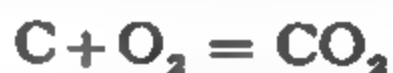
$$2\text{K}_4\text{Fe}(\text{CN})_6 + 3\text{ZnCl}_2 = \text{Zn}_3\text{K}_2(\text{Fe}(\text{CN})_6)_2 + 6\text{KCl}.$$
 Calculate the percentage of zinc in the ore.

CHAPTER VII

THERMOCHEMISTRY

HEAT OF REACTION

It is a matter of common experience that heat is given out in many chemical reactions. Thus the reaction:—



is chiefly important, not because carbon may be made to combine with oxygen to form carbon dioxide, but because energy is given out in the form of heat and can be used for warming purposes or converted into mechanical energy by means of engines.

This is not an isolated example of a reaction that produces heat, oxidation as a rule has this effect and heat production can be demonstrated in coal dust or in damp hay. In other cases, too, heat is absorbed during a reaction and the temperature of the reacting substances falls below that of their surroundings. In general an evolution or absorption of heat accompanies a chemical reaction. If heat is given out, the reaction is said to be *exothermic*, if heat is absorbed it is *endothermic*. Chemical reaction thus causes a *redistribution of energy* as well as of matter. Evolution or absorption of heat is not necessarily a sign of chemical reaction, as there is heat produced or used in many physical processes, such as evaporation, melting, solution, transformation from one modification into another.

The ordinary chemical equation such as that above represents only the redistribution of matter, but takes no account of that of energy; it is governed by the law of conservation of mass which states that the total mass of

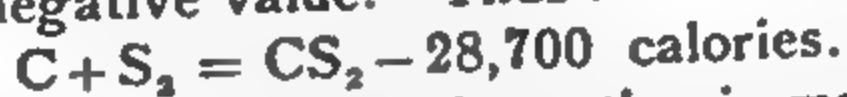
the products of the reaction must be the same as the total mass of the reacting substances. There is, however, also the *law of conservation of energy* according to which the amount of energy before the reaction is equal to that after the reaction. In order to show the obedience of a reaction to the law of conservation of energy, a *thermochemical equation* may be written thus:—



where Q represents the heat absorbed or (in this case) evolved in a reaction. Such an equation represents the redistribution of energy as well as of matter during the reaction.

Just as the ordinary chemical equation has a quantitative significance, so has the thermochemical equation, the value of Q being constant for any given reaction. The rate at which a chemical reaction is allowed to take place has no effect on the total amount of heat consumed or produced.

The unit of heat is the calorie, or gram calorie, which is the amount of heat necessary to raise the temperature of 1 gram of water 1° Centigrade at 15°C. Often, too, the kilogram calorie is used; it is the heat required to raise the temperature of 1 kilogram of water one degree Centigrade and is thus equal to 1,000 gm. calories. While in physical measurements the unit of weight is 1 gram, in chemistry 1 molecular weight of the substance under consideration is naturally selected. Thus in the example above, Q has the value, 96,400 calories. This means that on the combustion of 12 grams of carbon to form 44 grams of carbon dioxide, 96,400 calories of heat (enough heat to raise the temperature of 96,400 gm. of water one degree Centigrade) are evolved. 96,400 calories is known as the *heat of reaction* for the equation. If heat had been absorbed, the heat of reaction would, of course, have had a negative value. Thus:—



The measurement of heats of reaction is made by means of a calorimeter, in which the reaction is made to take place in a small vessel which can be placed inside another

containing water. The heat produced or consumed in the reaction is measured by the change in temperature of the known weight of water in the outer vessel.

The heat of reaction for the neutralisation of an acid by a base is usually expressed in terms of equivalent instead of molecular quantities. *The heat of neutralisation* is thus defined as that amount of heat which is evolved on neutralising an acid with a base in dilute solution with the formation of one gram equivalent of neutral salt. In accordance with the law of conservation of energy, when a reaction is capable of reversal, the addition of that amount of heat which it develops on going to completion in one direction will exactly suffice to drive it in the opposite direction. The heat that is added being simply used to restore the amount of energy to its original value. Thus the combination of mercury and oxygen has a heat of reaction of +30,600 cals.



The decomposition of mercuric oxide will thus be an endothermic reaction in which 30,600 cals are absorbed.

INTRINSIC ENERGY

Since the union of elements, such as between mercury and oxygen or between carbon and oxygen, can take place with the evolution of heat, it is evident that the elements themselves possess a certain amount of energy termed their intrinsic energy. The total intrinsic energy possessed by any particular element cannot be determined, but this is of little importance as we are concerned only with the differences of energy in thermochemical considerations. The intrinsic energy associated with each element is arbitrarily taken as the zero. When an element has several allotropic modifications there is a measurable difference in the intrinsic energies of the different forms. In such a case the energy content of the commonest form (e.g., rhombic sulphur, yellow phosphorus) is taken as zero. In the equation:—



the heat of reaction is 136,800 calories. Therefore for every molecule of water produced, 68,400 calories of heat will be evolved. The heat evolved (or absorbed) in the formation of one gram molecule of a compound from its elements is known as *the heat of formation* of the compound. Thus the heat of formation of water is 68,400 cal. In most cases heat is evolved and the compound (like the reaction) is termed exothermic, otherwise heat is absorbed and the compound (like the reaction) is endothermic.

Now let us suppose that the heat of formation of a substance AB is Q , calories or

$$A + B = AB + Q,$$

and let x be the intrinsic energy of one gm. molecule of the compound AB . The intrinsic energies of the elements A and B are, by definition, zero. If now the law of conservation of energy is valid, then the total amount of energy before and after the reaction will be the same; hence for $A + B = AB + Q$,

$$0 + 0 = x + Q,$$

$$x = -Q \text{ calories.}$$

This means that the intrinsic energy of a compound has the same magnitude as its heat of formation, but with the sign reversed.

Example. On the interaction of one molecule of sulphur trioxide with water to form sulphuric acid, 21,320 calories of heat are evolved. If the heat of formation of anhydrous sulphuric acid is 192,000 calories and that of water is 68,400 calories, calculate the heat of formation of sulphur trioxide



Then if x = the intrinsic energy of SO_3

$$x - 68,400 = -192,000 + 21,320$$

$$\therefore x = -103,180 \text{ calories}$$

and the heat of formation of SO_3 \therefore +103,120 cal.

PHYSICAL HEAT EFFECTS

In order to make a thermochemical equation quite definite, the physical state of the participating substances must be indicated; thus:—

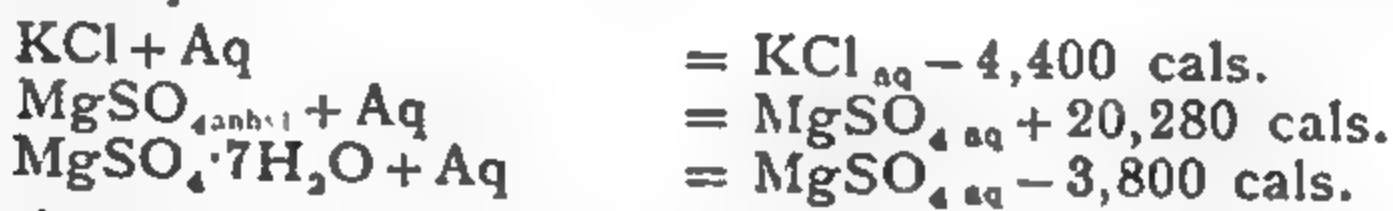


means that 58,700 calories of heat are evolved in the formation of one gram molecule of steam from gaseous hydrogen and oxygen. If the water condenses to the liquid state its (molecular) *latent heat of condensation* will be given out (i.e., the heat liberated on the condensation of 18 grams of steam = 9,700 calories) and this will naturally be associated with the heat of formation of the water. On the formation of 1 gram molecule of liquid water from gaseous hydrogen and oxygen, therefore $58,700 + 9,700 = 68,400$ calories of heat will be evolved. This may be expressed,

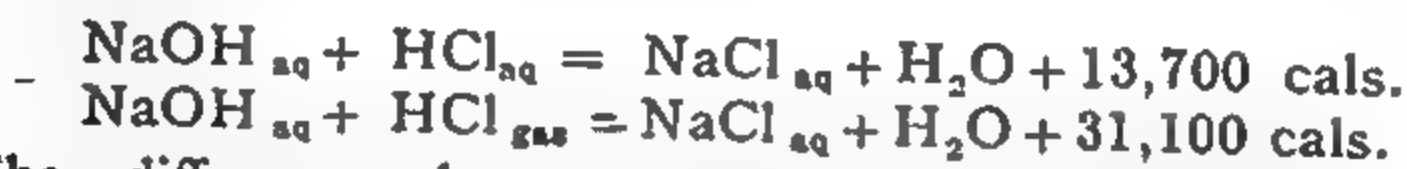


Similar adjustments have to be made for latent heats of fusion and for the heats of transformation of one variety of a substance into another.

When substances dissolve in water there is always an energy change, the amount of heat liberated or absorbed on solution of one gram molecule of substance in excess of water being known as its *heat of solution*. In the same way as in the case of latent heats, the heat of solution of a substance must be taken into account when reactions in solutions are considered. Heats of solution may be expressed:—



The importance of the heats of solution in calculations involving solutions is shown by the two following equations:—



The difference between these two heats, namely, $31,100 - 13,700 = 17,400$ calories actually represents the heat given out by one molecule of hydrochloric acid dissolving in water. The heat of solution of an electrolyte can be shown to be due to two effects, the actual energy required to separate the ions from the crystal lattice (lattice energy) and the work of separation of the ions

in the solution; the heat of solution has thus some dependence on concentration.

THE LAW OF HESS

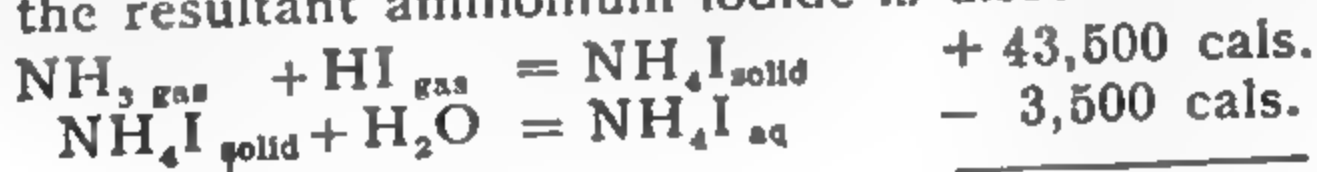
The law of constant proportions states that if a compound is prepared in more than one way, its material composition is constant and independent of the method of preparation. The same is true of its energy content, the intrinsic energy being independent of the method of formation. This may be extended to chemical reactions in general and the law of Hess states that when a chemical change takes place, the total heat absorbed or evolved is the same, no matter what intermediate reactions there may have been, provided, of course, that no form of energy other than heat has been evolved or absorbed.

If the system *A* changes to the system *B* with a heat evolution *Q*,



then *Q* is constant and independent of the method of carrying out the change. The law of Hess is a simple consequence of the law of conservation of energy.

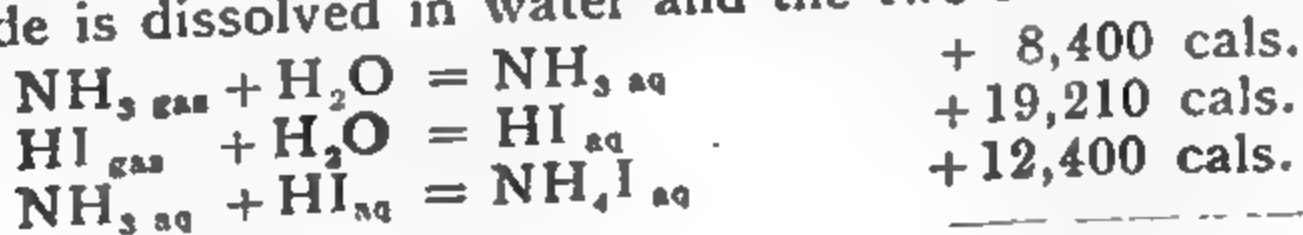
As an example we shall consider heat effects of the reaction between ammonia gas, hydrogen iodide gas and water to form ammonium iodide solution, the reaction being carried out in two ways. Firstly, if the gases unite and the resultant ammonium iodide is dissolved in water



making a total change of

+ 40,000 cal.

Secondly, if ammonia gas is dissolved in water, hydrogen iodide is dissolved in water and the two solutions mixed,



making a total of

+ 40,010 cal.

The difference between the amounts of heat evolved in carrying out the reaction in two different ways is thus only 10 calories, a quantity within the limit of the experimental error of the determinations involved.

INDIRECT DETERMINATION OF THE HEAT OF FORMATION

The law of Hess is of great use in determining the heats of formation of compounds for which this cannot be directly measured; this is the case especially with organic compounds for which the only quantity which is easily available for thermochemical measurement is the heat of combustion of the substance to carbon dioxide and water.

Example. Determine the heat of formation of formic acid from the following data:—

heat of combustion of formic acid	= 62,900 cal.
heat of formation of carbon dioxide	= 96,600 cal.
heat of formation of water	= 68,400 cal.



Now the heat given out in the formation of $\text{CO}_2 + \text{H}_2\text{O}$ from their elements is $96,600 + 68,400 = 165,000$ cal.

This means that the formation of $\text{CO}_2 + \text{H}_2\text{O}$ contributes 165,000 cal. out of the 62,900 evolved in the combustion, leaving -92,100 cal. resulting from the decomposition of formic acid.

Now the decomposition of 1 gm. mol. of formic acid is accompanied by an absorption of 92,100 cal. of heat, hence the formation of 1 gm. mol. of formic acid must be accompanied by an evolution of 92,100 calories.

\therefore heat of formation of formic acid is +92,100 cal.

As the total amount of energy before the reaction must be equal to that after the reaction, the sum of the intrinsic energies of the reacting substances must be equal to the sum of the intrinsic energies of the resultants plus the heat of reaction.

Thus in the example above:—



Now the intrinsic energy of a compound is of the same magnitude as its heat of formation but with reverse sign.

\therefore -heat of formation of $\text{HCOOH} = -\text{heat of formation of CO}_2 - \text{heat of formation of H}_2\text{O} + 62,900$ cal.

or heat of formation of $(\text{CO}_2 + \text{H}_2\text{O})$ —heat of formation of $\text{HCOOH} = 62,900$ cal.

Or generally, the heat of reaction = the sum of the heats of formation of the products—the sum of the heats of formation of the reactants.

The easiest method of calculation of heats of formation or reaction is by means of this restatement of the law of conservation of energy.

e.g., in the above example, if x = the heat of formation of formic acid:

heats of formation of the products—heats of formation of re-

actants = heat of reaction

$$96,600 + 68,400 - x = 62,900$$

$$\text{or } x = 165,000 - 62,900 = 92,100 \text{ cal.}$$

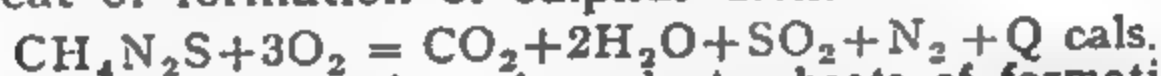
Example. Calculate the heat of formation of thiourea from the following data formation of :—

heat of combustion of thiourea = 341,900 cal.

heat of formation of water = 68,400 cal.

heat of formation of carbon dioxide = 96,400 cal.

heat of formation of sulphur dioxide = 71,100 cal.



Heats of formation of products—heats of formation of reactants
= heat of reaction



$$96,400 + 2 \times 68,400 + 71,100 + 0 - x = 341,900$$

$$\therefore x = 96,400 + 2 \times 68,400 + 71,100 - 341,900$$

$$= -37,400 \text{ cal.}$$

Example. Calculate the heat of formation of sodium monoxide from the following data :—

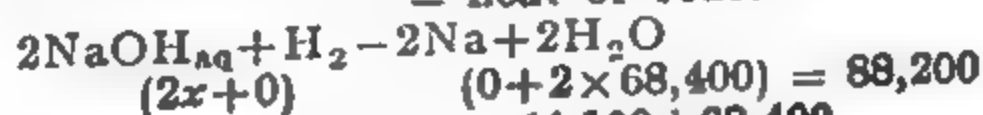


heat of formation of liquid water = 68,400 cal.

The heat of formation of one molecule of sodium hydroxide in solution should first be calculated. Let x = the heat of formation of NaOH_{aq} .



heats of formation of products—heats of formation of reactants
= heat of reaction



$$(2x + 0) \quad (0 + 2 \times 68,400) = 88,200$$

$$x = 44,100 + 68,400$$

$$= 112,500 \text{ cal.}$$

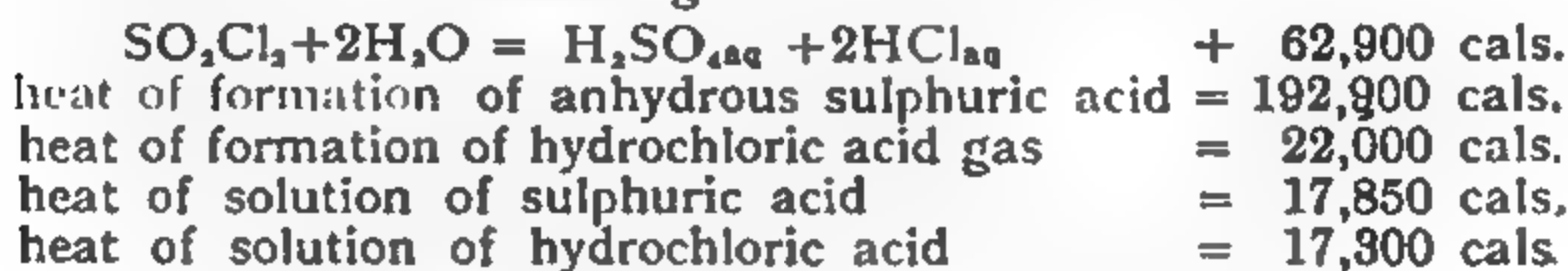
This may now be applied in the second equation to determine the heat of formation of sodium monoxide (y).



Heats of formation of products—heats of formation of reactants
= heat of reaction

$$\begin{aligned} 2\text{NaOH}_{\text{aq}} & \quad \text{Na}_2\text{O} + \text{H}_2\text{O} \\ (2 \times 112,500) & - (y + 68,400) = 56,500 \\ y & = 225,000 - (68,400 + 56,500) \\ & = 100,100 \text{ cal.} \end{aligned}$$

Example. Determine the heat of formation of sulphuryl chloride from the following data:—



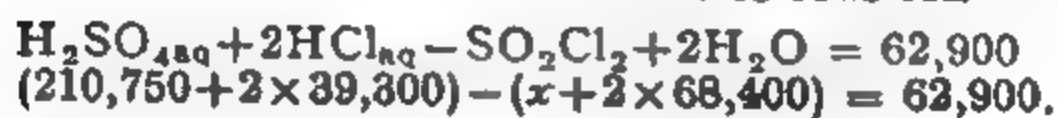
$$\therefore \text{heat of formation of } \text{H}_2\text{SO}_{4\text{aq}} = 210,750 \text{ cal.}$$



$$\therefore \text{heat of formation of } \text{HCl}_{\text{aq}} = 39,300 \text{ cal.}$$



Heats of formation of products—heats of formation of reactants
= heat of reaction



$$\therefore x = 89,650 \text{ cal.}$$

INDIRECT DETERMINATION OF HEATS OF REACTION

The law of Hess may also be applied to the calculation of heats of reaction and other thermal effects when these cannot be measured directly. Thus the heat of transformation of one allotropic modification of an element into another, or of one isomeric form of a compound into another may be calculated from the heats evolved when both forms are made to react separately with a common substance.

Example. The heat of formation of hydrogen selenide from amorphous selenium and hydrogen is $-19,400$ cal. and from metallic selenium and hydrogen, $-25,100$ cal.

Calculate the heat of transformation of amorphous to metallic selenium.

The heat of formation of H_2Se from amorphous Se is $-19,400$ cal.

\therefore the intrinsic energy of H_2Se is $+19,400$ cal. more than that of amorphous Se.

The heat of formation of H_2Se from metallic Se is $-25,100$ cal.

\therefore the intrinsic energy of H_2Se is $+25,100$ cal. more than that of metallic Se.

\therefore intrinsic energy of amorphous Se is $25,100 - 19,400 = 5,700$ cal. more than that of metallic Se.

and the transformation $\text{Se (amorphous)} \rightarrow \text{Se (metallic)}$ would be accompanied by the evolution of $5,700$ calories of heat.

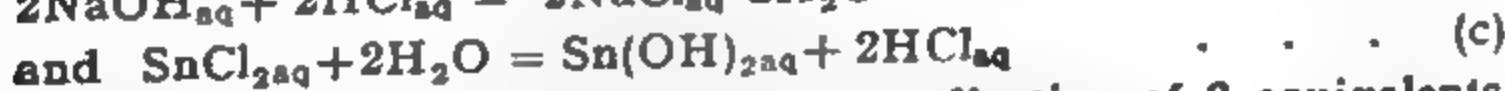
It is often difficult to make direct measurements of the heat of neutralisation of the bases of heavy metals as these may be soluble in acids, only with difficulty and the reactions do not lead to the complete formation of neutral salts owing to hydrolysis. In these cases therefore and in other reactions which do not go to completion, the heat of reaction must be calculated indirectly.

Example. The decomposition of one gram molecule of stannous chloride by sodium hydroxide in dilute aqueous solution is accompanied by an evolution of $24,700$ cal. of heat. The heat of neutralisation of one equivalent of sodium hydroxide by hydrochloric acid is $13,700$ cal. Calculate the heat of neutralisation of a gram equivalent of hydrochloric acid with stannous hydroxide.

The decomposition of stannous chloride by sodium hydroxide may be written:—



Now this reaction can be regarded as taking place in two stages,



Of these (c) is the reverse of the neutralisation of 2 equivalents of HCl by Sn(OH)_2 and the heat relations of (a) and (b) are given. Let x = the heat of neutralisation of 1 gram equivalent of HCl by Sn(OH)_2 then in reaction (c) $-2x$ cal. of heat are evolved.

In reaction (b) $2 \times$ the heat of neutralisation = $2 \times 13,700 = 27,400$ cal. are evolved and in reaction (a) 24,700 cal.

Now, by the law of Hess, the heat evolved in (a) = heat evolved in (b) + (c)

$$\therefore 24,700 = 27,400 - 2x$$

$$x = 1,350 \text{ cal.}$$

The heat of neutralisation of one gram equivalent weight of hydrochloric acid by stannous hydroxide is thus 1,350 cal.

PROBLEMS ON THERMOCHEMISTRY

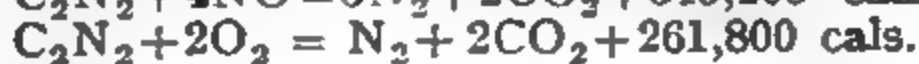
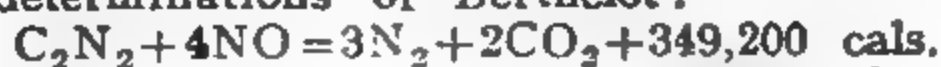
(The answers to problems with odd numbers will be found at the end of the book)

- 391 What weight of water could be converted from ice at 0°C . to steam at 100°C . by the combustion of 1,000 litres of hydrogen at N.T.P.? Heat of combustion of hydrogen = 68,400 cal.; latent heat of fusion of ice = 79 cal./gm.; latent heat of vaporisation of water = 539.0 cal./gm.
- 392 The heat of combustion of ammonia is 91,000 cal.; the heat of formation of water is 68,400 cal. Calculate the heat of formation of ammonia.
- 393 The heat of combustion of cyanogen is 262,000 cal.; the heat of formation of carbon dioxide is 96,400 cal. Calculate the heat of formation of cyanogen.
- 394 What weight of water could be converted into steam at 100°C . from 18°C . by the combustion of 5 Kgm. of coke containing 89% carbon, the rest being ash. Heat of combustion of carbon = 97,300 cal.
- 395 Determine the heat of formation of carbon dioxide from the following data:—
- | | |
|--|--------------------------|
| wt. of carbon burnt | = 10 gm. |
| wt. of H_2O in calorimeter | = 8.4 Kgm. |
| initial temp. | = 12°C . |
| final temp. | = 21.5°C . |
| water equivalent of calorimeter | = 160 cal. |
- 396 Calculate the heat of reaction of $\text{Cu} + \text{N}_2\text{O} = \text{CuO} + \text{N}_2 + \text{Q}$ cal. The heat of formation of N_2O is $-17,700$ cal., that of CuO is $+37,200$ cal.
- 397 What is the heat of the reaction $\text{PCl}_3 + \text{H}_2\text{O} = \text{POCl}_3 + 2\text{HCl}$, given the following heats of formation: $\text{PCl}_3 = 107,000$ cal.; $\text{POCl}_3 = 145,000$ cal.; $\text{HCl} = 22,000$ cal.; $\text{H}_2\text{O} = 58,100$ cal.
- 398 Calculate the heat of the reaction $\text{B}_2\text{O}_3 + 3\text{Mg} = 3\text{MgO} + 2\text{B}$. The heat of formation of $\text{B}_2\text{O}_3 = 272,600$ cal., that of $\text{MgO} = 143,300$ cal.

- 399 The heat of combustion of diamond is 94,430 cal., that of graphite 94,260 cal., and of amorphous carbon is 96,700 cal. Calculate the heat of transformation of amorphous carbon to diamond and to graphite.
- 400 The heat of formation of phosphorus nitride P_3N_3 was found by Stock to be 81,500 cal. from white phosphorus and 70,400 cal. from red phosphorus. Calculate the heat of transformation of white to red phosphorus.
- 401 Calculate the weight of water that could be raised 40°C . by burning the acetylene obtainable from 100 gm. of carbide on treatment with water. The heat of combustion of acetylene is 312,000 cal.
- 402 Both benzene and dipropargyl have the formula C_6H_6 . The heat of combustion of benzene vapour is 788,000 cal. and that of dipropargyl vapour is 854,000 cal. The heat of formation of water is 68,400 cal. and that of CO_2 96,400 cal. Compare the heats of formation of the two hydrocarbons.
- 403 The heat of formation of water vapour is 58,100 cal., that of carbon dioxide is 97,300 cal. The heat of combustion of oxalic acid to liquid water and CO_2 is 69,900 cal. If the latent heat of water is 9,700 cal. per gm. molecule, calculate the heat of formation of oxalic acid.
- 404 The heat of combustion of a molecular weight of acetone vapour is 437,300 cal., the heat of formation of water is 68,400 cal. and that of carbon dioxide is 96,400 cal. Calculate the heat of formation of acetone.
- 405 The heats of formation of anhydrous magnesium sulphate is 302,310 cal. and its heat of solution is +20,280 cal. The heats of solution of hydrates containing 1, 4, 6 and 7 molecules of water of crystallisation are +13,300, +4,330, -100 and -3,800 cal. respectively. Calculate the heats of hydration of these hydrates.
- 406 Phthalic acid ($C_8H_6O_4$) has a heat of combustion = 771,800 cal.
 $2H_2 + O_2 = 2H_2O + 136,800$ cal.
 $C + O_2 = CO_2 + 96,400$ cal.
 Calculate the heat of formation of the acid.
- 407 Calculate the heat of formation of pyridine C_5H_5N from the following data:—
 Heat of formation of water = 68,400 cal.
 heat of formation of carbon dioxide = 96,400 cal.
 heat of combustion of pyridine = 659,000 cal.
- 408 Veronal ($C_8H_{12}O_3N_2$) has a heat of combustion = 4,122,000 cal. The heats of formation of carbon dioxide and of water are 96,400 cal. and 68,400 cal. respectively. Calculate the heat of formation of veronal.

- 409 From the following data determine the heat of formation of anhydrous hydrochloric acid :—
 heat of neutralisation of hydrochloric acid by caustic soda = 13,780 cal.
 heat of formation of aqueous caustic soda = 111,800 cal.
 heat of formation of sodium chloride = 97,700 cal.
 heat of solution of sodium chloride = -1,200 cal.
 heat of formation of water = 68,400 cal.
 heat of solution of hydrochloric acid = 17,300 cal.
- 410 From the following data calculate the heat of formation of anhydrous lithium sulphate :—
 Heat of neutralisation of 1 equivalent of sulphuric acid by LiOH = 15,640 cal.
 heat of formation of aqueous lithium hydroxide = 121,600 cal.
 heat of formation of anhydrous H_2SO_4 = 192,900 cal.
 heat of solution of lithium sulphate Li_2SO_4 = 6,050 cal.
 heat of formation of water = 68,400 cal.
 heat of solution of sulphuric acid = 17,850 cal.
- 411 Calculate the heat of formation of carbonyl sulphide from the following data :—
 heat of combustion of carbonyl sulphide = 131,000 cal.
 heat of formation of carbon dioxide = 96,400 cal.
 heat of formation of sulphur dioxide = 71,000 cal.
- 412 Phenol mustard oil has the formula $\text{C}_7\text{H}_5\text{NS}$ and evolves 1,024,300 cal. on the combustion of one gm. molecule. The heats of formation of carbon dioxide, water and sulphur dioxide are 96,400, 68,400 and 71,100 cal. respectively. Calculate the heat of formation of the compound.
- 413 Calculate the heat of formation of hexachlorobenzene (C_6Cl_6) from the following data :—
 heat of combustion of hexachlorobenzene = 509,000 cal.
 heat of formation of carbon dioxide = 96,400 cal.
- 414 From the following data calculate the heat of formation of anhydrous sulphuric acid :—
 heat of neutralisation of 1 gm. equivalent of sulphuric acid by sodium hydroxide = 15,700 cal.
 heat of formation of aqueous caustic soda = 111,800 cal.
 heat of formation of sodium sulphate = 328,600 cal.
 heat of solution of sodium sulphate = 780 cal.
 heat of formation of water = 68,400 cal.
 heat of solution of sulphuric acid = 17,850 cal.
- 415 Methyl mercaptan (CH_3S) has heat of combustion = 298,800 cal. The heats of formation of water, CO_2 and of sulphur dioxide are 68,400 cal. 96,400 cal. and 71,000 cal. respectively. Calculate the heat of formation of the mercaptan.

- 416 Calculate the heat of formation of NO from the following determinations of Berthelot:—



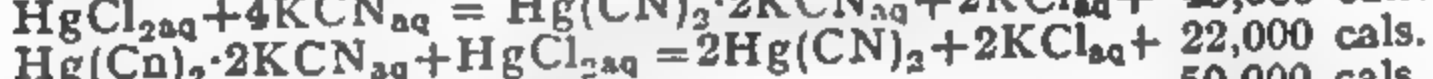
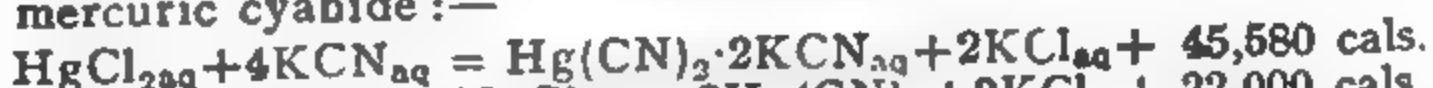
- 417 Calculate the heat of formation of phosphorus oxybromide from the following data:—



- 418 Calculate the heat of formation of anhydrous cobalt chloride from the following data:—



- 419 From the following data determine the heat of formation of mercuric cyanide:—



- 420 Calculate the heat of formation of anhydrous aluminium chloride from the following data:—



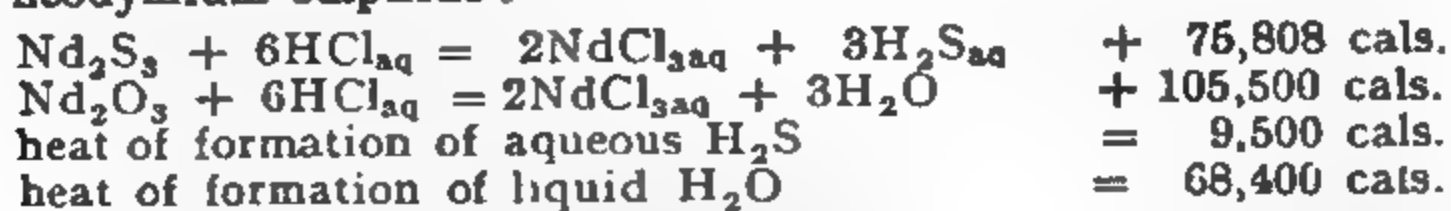
- 421 Calculate the heat of formation of $\text{Mg}_2\text{S}_2\text{O}_8 \cdot 6\text{H}_2\text{O}$ from the following data:—



- 422 67,600 cal. of heat are evolved in the interaction of one molecular weight of sodium peroxide with zinc to form sodium zincate; the heat of formation of sodium peroxide is 119,800 cal. Calculate the heat of formation of sodium zincate.

- 423 The heats of formation of sodium tungstate, sodium peroxide and sodium monoxide are 389,200 cal., 119,800 cal. and 100,700 cal. respectively. What amount of heat is given out by the formation of one molecule of sodium tungstate from metallic tungsten and sodium peroxide?

- 424 From the following data calculate the heat of formation of neodymium sulphide:—



also on burning metallic neodymium in air to form one molecule of Nd_2O_3 , 435,100 cal. are evolved.

- 425 The heat evolved in the formation of one gm. molecule of silver oxide from silver fluoride and caustic potash in aqueous solution is 17,600 cal. The heat of neutralisation of hydrofluoric acid by caustic potash is 16,100 cal. Calculate the heat of neutralisation of silver oxide by hydrofluoric acid.
- 426 The heat of decomposition of one gm. molecule of manganese chloride by potassium carbonate in aqueous solution is -4,000 cal. The heat of neutralisation of one gm. equivalent of manganese hydroxide ($\text{Mn}(\text{OH})_2$) by carbonic acid is 6,615 cal., that of potassium hydroxide by carbonic acid is 10,100 cal. and that of potassium hydroxide by hydrochloric acid is 13,750 cal. Calculate the heat of neutralisation of manganese hydroxide by hydrochloric acid.
- 427 The heat evolved in the decomposition of one gm. molecule of nickel sulphate by barium hydroxide is 10,630 cal. The heat of neutralisation of one gm. equivalent of barium hydroxide by sulphuric acid is 18,400 cal. Calculate the heat of neutralisation of one gm. equivalent of nickel hydroxide by sulphuric acid.
- 428 The heat evolved on the decomposition of one gm. molecule of chromium fluoride in caustic soda solution is 23,700 cal., the heat of neutralisation of caustic soda by hydrofluoric acid is 16,270 cal. Calculate the heat of neutralisation of one gm. equivalent of chromium hydroxide by hydrofluoric acid.
- 429 The decomposition of one gm. molecular weight of cadmium sulphate by barium hydroxide in aqueous solution results in the evolution of 13,070 cal. of heat. The heat of neutralisation of a gm. equivalent of barium hydroxide by sulphuric acid is 18,400 cal. Calculate the heat of neutralisation of cadmium hydroxide by sulphuric acid.
- 430 The heat of decomposition of one gm. molecular weight of zinc sulphate by barium hydroxide in aqueous solution is 5,770 cal. The heat of neutralisation of one gm. equivalent of barium hydroxide by sulphuric acid 8,450 cal. Calculate the heat of neutralisation of zinc hydroxide by sulphuric acid.

MISCELLANEOUS PROBLEMS

(Answers to those problems with odd numbers will be found at the end of the book)

- 431 31 c.c. of a mixture of nitrous oxide and oxygen were mixed with 50 c.c. of hydrogen and passed through a heated platinum capillary to effect combustion. The volume contracted to 28 c.c. What was the volume of nitrous oxide in the mixture?
- 432 0.128 gm. of a substance is vaporised in the Victor Meyer apparatus, expelling 31.7 c.c. of air, measured over water at 18° and 768 mm. If the normal molecular weight of the substance is 162, and each molecule dissociates into three dissociated molecules on complete dissociation, calculate the degree of dissociation of the substance.
- 433 A gaseous organic compound containing 38.71% of carbon, 16.13% of hydrogen and 45.16% of nitrogen has a rate of diffusion 0.254 times that of hydrogen. What is its molecular formula?
- 434 A mixture of helium and nitrogen containing 10% of helium is passed through a porous tube. What is the percentage of helium in the gas diffusing through the tube? What would be the composition of the gas after four such treatments?
- 435 Sulphur fluoride contains 21.9% of sulphur. If 47.5 c.c. of sulphur fluoride diffuse through an aperture in the same time as 86.5 c.c. of carbon dioxide, what is the molecule formula of sulphur fluoride?
- 436 100 c.c. of a gaseous hydrocarbon containing 85.8% of carbon diffuse through a porous plug in the same time as 98 c.c. of carbon dioxide. What would be the weight of 1 litre of the gas at 15° and 740 mm. pressure?
- 437 Find the vapour density of a substance, 0.114 gm. of which displaced 30.9 c.c. of air from a Victor Meyer apparatus, measurement being made over water at 15° and 760 mm. pressure.
- 438 A bulb used for a Dumas vapour density experiment weighed, full of air, 33.146 gm. Sealed, full of aluminium chloride vapour at 300° and 750 mm., it weighed 33.926 gm. The weight of the bulb filled with water was 213.1 gm. On treatment of 0.157 gm. of aluminium chloride with silver nitrate, 0.5050 gm. of silver chloride were obtained. Determine the molecular complexity of aluminium chloride.
- 439 When 0.1045 gm. of a natural oil is vaporised in a Victor Meyer apparatus, 18.8 c.c. of air (moist, at 17° and 754 mm. pressure) are expelled. Find the molecular weight of the substance.

- 440 50 c.c. of a mixture of carbon dioxide, hydrogen and ethylene contracted on treatment with caustic potash to 26 c.c. 50 c.c. of oxygen were added. After sparking, the volume was 31 c.c., and contracted to 7 c.c. on further treatment with potash. What was the composition of the mixture?
- 441 15 c.c. of hydrogen were added to 25 c.c. of a mixture of nitrous oxide and nitrogen, and the gas passed through a heated platinum capillary. The volume contracted to 30 c.c. Find the proportion of nitrous oxide in the original gas.
- 442 A glass bulb (volume 360 c.c.) containing oxygen at N.T.P. weighs 10.9541 gm. Filled with ozonised oxygen at N.T.P., its weight is 10.9644 gm. Calculate the percentage of ozone in the gas. If the ozonised oxygen were passed through potassium iodide and the solution acidified, what volume of 0.91 *N*/10 sodium thiosulphate would be required to titrate the liberated iodine?
- 443 How much oxygen, measured at 15° and 750 mm. would be required for the combustion of 50 c.c. of arsenic hydride (at N.T.P.). How much 0.981 *N*/10 iodine solution would be required to oxidise the oxide of arsenic formed?
- 444 Boron trichloride is hydrolysed by water to hydrochloric acid and boric acid, which does not react with sodium carbonate. 1240 c.c. of a mixture of boron trichloride vapour and hydrogen chloride gas, measured dry at 40°C. and 760 mm. pressure is absorbed in 200 c.c. of 0.530 *N* sodium carbonate solution. 27.2 c.c. of *N*/5 sulphuric acid were required to titrate the excess sodium carbonate, using methyl orange as indicator. Calculate the composition of the gas, by volume, and the volume of carbon dioxide at 20° and 740 mm. which it liberates from the sodium carbonate solution.
- 445 0.6703 gm. of a compound of cobalt chloride and ammonia were heated with concentrated caustic potash and the ammonia evolved led into 25 c.c. of *N*/2 sulphuric acid. 9.86 c.c. of 1.015 *N*/10 sodium hydroxide were required to neutralise the excess acid. By evaporation of 0.477 gm. of the compound with sulphuric acid, 0.3165 gm. of cobalt sulphate were obtained. Find the formula of the compound.
- 446 2,500 c.c. of a gas (measured at N.T.P.) containing hydrogen chloride were led through a bubbler containing 25 c.c. of 0.99 *N*/2 sodium hydroxide. 9.6 c.c. of *N*/2 sulphuric acid were subsequently needed to titrate the excess alkali. What was the concentration of hydrogen chloride in the gas?
- 447 2.285 gm. of a mixture of zinc oxide and zinc carbonate were dissolved in 50 c.c. of normal hydrochloric acid. 9.83

c.c. of 0.995 $N/2$ sodium hydroxide were needed to neutralise the excess acid. Find the proportion of zinc oxide in the mixture.

- 448 The solution obtained by treating 1.760 gm. of sodium amalgam with water neutralised 18.75 c.c. of 1.02 $N/10$ sulphuric acid. What percentage of sodium did the amalgam contain?
- 449 1.1 gm. of a mixture of anhydrous borax and caustic soda were dissolved in water and titrated with 1.1 $N/2$ sulphuric acid, using methyl orange as indicator. 22.7 c.c. of acid were required. Find the percentage of caustic soda in the mixture.
- 450 10.24 gm. of crude sodium carbonate crystals, contaminated with sodium sulphate and sodium hydroxide, were dissolved in water and the solution made up to 250 c.c. 50 c.c. of the solution titrated with 1.15 $N/2$ sulphuric acid required 13.64 c.c. of acid, using phenolphthalein as indicator, 25.3 c.c. using methyl orange. Find the composition of the sample taken.
- 451 In the analysis of a manganese steel, the manganese in a 2.086 gm. sample was converted to permanganate, and the volume made up to 250 c.c. 25 c.c. of 1.004 $N/10$ ferrous sulphate solution required 47.2 c.c. of this solution for titration. Find the manganese content of the steel.
- 452 0.1024 gm. of pyrolusite were dissolved in 25 c.c. of 1.008 $N/10$ ferrous sulphate. The excess ferrous sulphate was titrated with 2.3 c.c. of 0.98 $N/10$ potassium permanganate solution. Find the percentage of manganese dioxide in the mineral.
- 453 0.2725 gm. of potassium persulphate ($K_2S_2O_8$) were dissolved in 25 c.c. of acidified 0.965 $N/10$ ferrous sulphate. 4.60 c.c. of $N/10$ potassium dichromate were required to titrate the excess ferrous iron. Find the percentage purity of the potassium persulphate.
- 454 0.754 gm of red lead, containing as impurity some lead peroxide, were heated with concentrated hydrochloric acid in a stream of carbon dioxide. The chlorine evolved was absorbed in potassium iodide solution, and the liberated iodine titrated with 23.33 c.c. of 0.99 $N/10$ sodium thio-sulphate. Find the percentage of PbO_2 in the red lead.
- 455 0.234 gm. of fluorine oxide were passed into an acid solution of potassium iodide, iodine being liberated, and water and hydrofluoric acid being formed. The solution was neutralised and made up to 250 c.c., 36.05 c.c. of the solution so made being required to react with 25 c.c. of $N/10$ thio-sulphate. The vapour density of fluorine oxide is 27. Deduce its molecular formula.

- 456 Iodic acid reacts with hydriodic acid thus:
 $\text{HIO}_3 + 5\text{HI} = 3\text{H}_2\text{O} + 3\text{I}_2$. 0.112 gm. of sodium iodate were added to excess potassium iodide and the solution acidified. The iodine liberated reacted with 30.13 c.c. of 1.093 *N*/10 sodium thiosulphate solution. Find the percentage purity of the sodium iodate.
- 157 The iodine liberated by addition to 25 c.c. of potassium dichromate solution to excess of acidified potassium iodide reacted with 24.2 c.c. of sodium thiosulphate solution. 26.3 c.c. of the same thiosulphate decolorised the iodine liberated by 25 c.c. of a solution containing 0.855 gm. of sodium iodate in 250 c.c. Find the normality of the potassium dichromate.
- 158 1.25 gm. of an impure sample of arsenious oxide were dissolved in sodium bicarbonate solution and made up to 250 c.c. 25 c.c. required 22.4 c.c. of 1.02 *N*/10 iodine for oxidation. What is the percentage purity of the arsenious oxide?
- 459 1 gm. of cadmium amalgam, dissolved in nitric acid and treated with hydrogen sulphide, yielded 1.1980 gm. of the mixed sulphides. What was the percentage composition of the amalgam?
- 460 1.8 gm. of a mixture of barium and magnesium carbonates gave on heating 450 c.c. of carbon dioxide, measured at 13° and 750 mm. pressure. Find the percentage of barium carbonate in the mixture.
- 461 0.5296 gm. of a specimen of cast iron were heated in a stream of pure oxygen. The gases were led through a tube of potassium hydroxide which increased in weight 0.0488 gm. Calculate the percentage of carbon in the cast iron.
- 462 1 gm. of a mixture of sodium and potassium hydroxides was dissolved in water and exactly neutralised with sulphuric acid. An excess of barium chloride was added, and the precipitate, after washing and igniting, weighed 2.496 gm. What was the proportion of sodium hydroxide in the mixture?
- 463 Treatment of 1 gm. of a mixture of calcium- and magnesium carbonates with hydrochloric acid yielded 258.5 c.c. of dry carbon dioxide at 15° and 755 mm. pressure. Find the composition of the mixture.
- 464 0.2424 gm. of hydrated nickel chloride were evaporated to dryness with sulphuric acid, 0.1576 gm. of nickel sulphate being obtained. How many molecules of water of crystallisation did the hydrated chloride contain?
- 465 An anthracite coal contains 92.7% of carbon, 3.4% of volatile matter, and 8.9% of ash. What quantity of heat would be evolved on complete combustion of 2 kg. of coal, if the heat of formation of carbon dioxide is 97,300 cal. per gm. mol., and if the volatile matter may be assumed to be methane, the heat of combustion of which is 212,000 cal. per gm. mol.?

- 466 The heats of formation of methane (CH_4), of carbon dioxide and of hydrogen chloride gas are 21,700, 97,300 and 22,000 cal. per gm. molecule respectively. The heat of combustion of methylene chloride, CH_2Cl_2 to carbon dioxide and hydrogen chloride gas is 106,800 cal. per gm. mol. What is the heat of the reaction leading to formation of methylene chloride: $\text{CH}_4 + 2\text{Cl}_2 = \text{CH}_2\text{Cl}_2 + 2\text{HCl}$?
- 467 The heats of formation of silica, silicon tetrachloride and carbon monoxide are 191,000, 122,000 and 28,600 cal. per gm. molecule respectively. What heat effect attends the formation of silicon tetrachloride by the action of chlorine on silica in the presence of carbon?
- 468 What is the heat of combustion of carbon disulphide in nitrous oxide, given that the heats of formation of carbon dioxide, sulphur dioxide, carbon disulphide and nitrous oxide are 97,300, 69,200, -28,700 and -17,700 cal. per gm. molecule respectively?
- 469 A natural gas contains 23% methane, 35% nitrogen, 40% hydrogen and 2% ethylene by vol. The heats of combustion, to steam and carbon dioxide, of hydrogen, methane and ethylene are 58,700, 212,000, and 333,400 cal. per gm. molecules respectively. The gas is burned under a boiler, fed with water at 15°C ., in which 5,000 kg. of water are to be evaporated under atmospheric pressure. The latent heat of steam is 540 cal. per gm. What volume of gas (at N.T.P.) must be supplied?
- 470 A Bessemer converter is charged with 9,000 kg. of iron containing 2.9% of carbon. How many cubic metres of air, containing 21% of oxygen, at 22° and 760 mm. pressure, must be supplied for the oxidation of all the carbon if one-third burns to carbon dioxide and the rest to carbon monoxide?
- 471 A certain gas reacts with an equal volume of water vapour in the presence of a catalyst to give carbon dioxide and hydrogen chloride in the proportions by weight of 36.5:60.6. What is the simplest formula of the gas?
- 472 Find what volume of sulphur dioxide, measured at 13° and 740 mm. pressure, will be oxidised by 50 c.c. of a solution of hydrogen peroxide containing 5 gm. of H_2O_2 per litre.
- 473 Anhydrous ferrous chloride and ammonia react to form a compound. 0.2041 gm. of ferrous chloride absorbed 235.1 c.c. of ammonia at 18.5° and 746 mm. pressure. Find the formula of the compound formed.
- 474 Atmospheric nitrogen is converted to ammonia, and this oxidised catalytically to ammonium nitrate. What volume of air (80% nitrogen) at N.T.P. must be liquefied and fractionated to make 1,000 kg. of ammonium nitrate, if 10% of the nitrogen is lost during the fractionation?

- 475 The fermentation of sugar proceeds according to the equation $C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$. What volume of carbon dioxide at N.T.P. would be generated during the production of 20,000 litres of absolute alcohol, of specific gravity 0.79?
- 476 6.5 gm. of a mixture of sodium hydroxide, potassium hydroxide and anhydrous sodium carbonate were dissolved in water and made up to 250 c.c. 25 c.c. of the solution required for neutralisation 19.5 c.c. of $N/2$ acid, using phenolphthalein as indicator, and 26.23 c.c., using methyl orange. Determine the percentage composition of the mixture.
- 477 0.320 gm. of hydrated barium peroxide were dissolved in cold water, acidified, and titrated with 0.97 $N/10$ potassium permanganate solution, of which 21.05 c.c. were decolorised. Find the number of molecules of water of crystallisation in the hydrate.
- 478 The gas evolved when 1 gm. of a mixture of ammonium nitrate and ammonium nitrite was heated occupied (dry) 341 c.c. at $20^\circ C$. and 765 mm. Find the percentage of ammonium nitrite in the mixture.
- 479 When 3.128 gm. of a mixture of sodium bromide and potassium bromide was evaporated to dryness with sulphuric acid, 2.221 gm. of the mixed sulphates were obtained. What was the composition of the mixture?
- 480 0.424 gm. of a compound of platinous chloride and ammonia left on ignition a residue of platinum weighing 0.276 gm. 1.81 gm. of the compound were heated with concentrated sulphuric acid, then made alkaline, and the ammonia distilled into 25 c.c. of $N/2$ sulphuric acid. The excess acid was neutralised by 4.0 c.c. of 1.037 $N/10$ sodium hydroxide. Find the empirical formula of the compound.
- 481 0.94 gm. of the anhydrous chloride of an element yielded 2.45 gm. of the sulphate, containing 51.4% of water of crystallisation. Determine the atomic weight of the metal, the specific heat of which is 0.263, and the number of molecules of water of crystallisation in the sulphate.
- 482 9.7 gm. of bleaching powder were ground up with water and the solution made up to 1 litre. 25 c.c. of the solution were added to excess potassium iodide, acidified, and then required 23.0 c.c. of 0.98 $N/10$ sodium thiosulphate for titration. Find the percentage of available chlorine in the bleaching powder.
- 483 2.105 gm. of hydrated ferric oxide were dissolved in acid and the solution made up to 250 c.c. 25 c.c. of the solution were reduced by means of stannous chloride, and titrated with $N/10$ potassium dichromate, requiring 23.7 c.c. Find the percentage of water in the hydrate.

- 484 An electric current was passed for 8 hrs. through a voltmeter filled with potassium iodide solution. The liquid around the anode was then removed, and its volume made up to 250 c.c. 25 c.c. of this solution were decolorised by 28.0 c.c. of 1.06 *N*/10 sodium thiosulphate. What was the average value of the current?
- 485 What would be the cost, per kilogram, of the electro-deposition of copper, if current is supplied at 110 volts at the price of $\frac{1}{2}$ d. per kilowatt-hour?
- 486 2.100 gm. of a mixture of cadmium and zinc chlorides were dissolved in water and the volume made up to 250 c.c. 25 c.c. of the solution required for titration 23.2 c.c. of 1.063 *N*/10 silver nitrate solution. What percentage of zinc chloride did the mixture contain?
- 487 2.5 gm. of a copper ore were brought into solution, and the volume made up to 250 c.c. 25 c.c. were withdrawn, treated with excess potassium iodide, and the liberated iodine titrated with 24.82 c.c. of 1.007 *N*/10 sodium thiosulphate. What was the copper content of the ore?
- 488 At a certain temperature, 85 c.c. of nitrogen peroxide diffuse through a porous plug in 485 secs. under the same conditions, 100 c.c. of carbon dioxide diffuse through in 433 secs. What is the degree of dissociation of the N_2O_4 ?
- 489 By the combustion of 0.1550 gm. of a compound of carbon, hydrogen and oxygen, 0.0504 gm. of water, and 0.3285 gm. of carbon dioxide were obtained. 0.741 gm. of the substance dissolved in 24.7 gm. of water, raised the boiling point 0.096° , the molecular elevation constant for water being 5.2° . Find the molecular formula of the compound.
- 490 Find the molecular weight of iodoform, 0.3195 gm. of which, dissolved in 19.6 gm. of benzene, depress the freezing point 0.212° . The depression constant of benzene = 51.2° per 100 gm. of benzene.
- 491 When the solution in water of 0.323 gm. of hydrated magnesium ammonium chloride was treated with silver nitrate, 0.541 gm. of silver chloride were obtained. 0.515 gm. of the compound yielded 0.241 gm. of magnesium sulphate on evaporation with sulphuric acid and gentle ignition. Find the formula of the double salt.
- 492 The loss in weight produced when 2.433 gm. of mixed sodium and potassium nitrates were heated with pure silica was 1.443 gm. What was the percentage of sodium nitrate?
- 493 The heat of reaction $C + H_2O = CO + H_2$ is $-29,500$ cal. The heat of formation of carbon monoxide, $C + \frac{1}{2}O_2 = CO$ is $29,200$ cal. per gm. molecule. If the thermal losses in a semi-water gas producer amount to 15%, in what proportions by volume should air (20% oxygen) and steam be admitted to the plant in order that the exothermic and endothermic reactions may just balance?

- 494 1.775 gm. of an aluminium alloy dissolved in potassium hydroxide with the liberation of 1,646 c.c. of hydrogen (at N.T.P.). What percentage of aluminium did the alloy contain?
- 495 What volume of air, containing 21% of oxygen, must be supplied to pyrites burners in order to roast 200 kg. of iron pyrites, the products being sulphur dioxide and ferric oxide?
- 496 2.11 gm. of a mineral containing calcium were brought into solution, and made up to a volume of 250 c.c. 50 c.c. were removed, the calcium precipitated with ammonium oxalate, and the washed precipitate dissolved in sulphuric acid. The solution was titrated with 26.8 c.c. of 0.96 *N*/10 potassium permanganate. Find the percentage of calcium oxide in the mineral.
- 497 Ethylene forms 80% of a gas made by cracking petroleum. How many cubic metres of cracked gas must be used for the manufacture of 10 kg. of alcohol by the catalytic process $C_2H_4 + H_2O = C_2H_5OH$?
- 498 1.441 gm. of potassium tetrathionate were treated with bromine water, all the sulphur being oxidised to sulphate. Addition of barium chloride yielded 4.450 gm. of barium sulphate. What is the percentage of sulphur in potassium tetrathionate?
- 499 The heats of formation of silver chloride and of anhydrous zinc chloride are 30.41 kg.-cals. and 97.2 kg.-cals. per gm. molecule respectively. The heat of solution of zinc chloride is 15.6 kg.-cals. per gm. mol. What heat effect attends the reduction of silver chloride by metallic zinc, in aqueous suspension?
- 500 The heats of formation of magnesium oxide and of chromic oxide Cr_2O_3 are 143,900 and 267,800 cal. per gm. molecule respectively. How much heat is evolved when 20 kg. of chromium are prepared by reduction of chromic oxide with magnesium powder?
- 501 Strontium metal is obtained by electrolysis of fused strontium chloride. What weight of metal can be obtained in 8 hours by the passage of a current of 5.6 amps.?
- 502 Acetic acid, $C_2H_4O_2$, is obtained from acetylene, C_2H_2 , by a catalytic process. What weight of acetic acid could be made from the acetylene generated from calcium carbide CaC_2 made from 1,000 kg. of limestone (98% $CaCO_3$)?
- 503 35 c.c. of hydrogen were added to 35 c.c. of a mixture of nitrogen, nitrous oxide and nitric oxide. The volume after passing the gases through a heated platinum capillary was 38 c.c. 10 c.c. of oxygen were added, and the gases passed again through the capillary. The new volume was 34.5 c.c. What was the composition of the original mixture?

- 504 Nitrogen is made by bubbling air through strong ammonia solution and leading the gases over red hot copper. Assuming that the mixture is such as just to oxidise the ammonia taken up, what volume of nitrogen is obtained from 5 litres of air containing 21% of oxygen?
- 505 The density of chlorine, relative to air, is 2.435. Neglecting the presence of gases other than 0.9% of argon, what value does this give for the relative proportions of nitrogen and oxygen in the air?
- 506 On treating 2 grams of a mixture of calcium and barium carbonates with hydrochloric acid, 0.591 gram of carbon dioxide was evolved. Calculate the percentage of barium carbonate present.
- 507 One litre of sodium hydroxide solution was exposed to the atmosphere. 25 c.c. of the resulting solution was titrated with 0.92 *N*/10 acid, the volumes required being 23.4 c.c. using phenolphthalein and 27.7 c.c. using methyl orange as indicator. What was the concentration of the original hydroxide solution and what volume of carbon dioxide did it absorb?
- 508 0.9 grams of the mixed carbonates of magnesium and barium gave on treatment with hydrochloric acid, 180 c.c. of carbon dioxide at N.T.P. Find the percentage proportions of the two carbonates.
- 509 Radium chloride crystals are isomorphous with those of barium chloride; 0.01462 g. of the crystallised salt, when dissolved in water and treated with silver nitrate solution, yielded 0.01259 g. of silver chloride. Calculate the atomic weight of radium.
- 510 What is the minimum weight of bleaching powder containing 32% of available chlorine, which will completely oxidise one gram of arsenious oxide (96%) to arsenic acid?
- 511 100 c.c. of the vapour of a liquid hydrocarbon containing 92.3% of carbon required for combustion 750 c.c. of oxygen. Calculate the volume of air which would be displaced by the vaporisation of 0.173 g. of the hydrocarbon in a Victor Meyer apparatus, assuming the air to be collected over water at 16°C. atmospheric pressure being 756 mm. (Water vapour pressure at 16° = 13.5 mm.)
- 512 In a recent determination of the atomic weight of tin, the following ratios of SnCl_4 ; Ag were found:—
- | | |
|-----------------|--------|
| SnCl_4 | Ag |
| 9.331 | 14.947 |
| 9.398 | 15.566 |
| 10.327 | 17.105 |
- Calculate the accurate atomic weight of tin.
- 513 0.484 g. of sodium sulphite crystals ($\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$) was added to 50 c.c. of standard iodine solution, the residual iodine requiring 12.80 c.c. of 1.04 *N*/10 thiosulphate for titration. 25 c.c. of the untreated iodine solution required

23.45 c.c. of the same thiosulphate. Calculates the percentage purity of the crystals.

- 514 How much oxygen at 15°C . and 760 mm. would be required for the complete combustion of 50 c.c. of arsenic hydride; and how much .981 $N/10$ iodine solution would be required to react with the oxide of arsenic formed?
- 515 A gaseous hydrocarbon contains 82.76% of carbon, and 20 c.c. on explosion with excess of oxygen give 80 c.c. of carbon dioxide. What is the formula of the hydrocarbon?
- 516 The sulphate of a metal A contains 22.78% of the metal, and is isomorphous with $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$. A second metal B comes below calcium and strontium in group II of the periodic table and its only equivalent is 68.68. Compare the specific heats of the two metals, assuming Dulong and Petits Law to be accurate in both cases.
- 517 A salt containing sodium, nitrogen and oxygen gave on analysis, $\text{Na} = 43.40\%$, $\text{N} = 26.41\%$. What could the substance be and what would be the percentage of silver in the silver salt?
- 518 0.67 g. of an iron ore are dissolved in dilute sulphuric acid and titrated with .973 decinormal KMnO_4 , 15.28 c.c. being required. The whole of the iron is then reduced to the ferrous condition, and again titrated, when 37.63 c.c. is required. Calculate the percentage of ferrous and ferric iron in the ore.
- 519 1.52 g. of a calcium mineral were dissolved in acid and the calcium precipitated with ammonium oxalate. The washed calcium oxalate precipitate was decomposed with dilute acid, the solution was made up to 250 c.c., and 50 c.c. portions were titrated with 1.06 $N/10$ potassium permanganate, 15.4 c.c. being required for each portion. Calculate the percentage of calcium in the mineral.
- 520 The element gallium can replace aluminium giving an alum in which 2.55 g. of gallium replace 1 g. of aluminium. Aluminium oxide contains 53.04% of aluminium and the specific heat of aluminium is 0.237. Determine from the above data the atomic weight of gallium.
- 521 10 c.c. of a mixture of ethane (C_2H_6) and carbon monoxide were exploded with an excess of oxygen. Potash absorbed 14 c.c. of the gases remaining after the explosion. Calculate the percentage composition of the mixture.
- 522 What volume of air at 15°C . and 765 mm. pressure, containing 20% of oxygen would be required for the complete combustion of 2 g. of carbon disulphide? If the products of the combustion were dissolved in water, how many c.c. of .980 N iodine solution are required to oxidise the sulphurous acid formed?

- 523 Define (a) exothermic compound, (b) endothermic reaction, (c) intrinsic energy of a compound, (d) heat of neutralisation. Calculate the heat of neutralisation of lithium hydroxide with sulphuric acid from the following data: heat of formation of $\text{H}_2\text{SO}_4 = 210.8 \text{ Kg. cal.}$; that of $\text{LiOH} = 121.8 \text{ Kg. cal.}$, that of $\text{H}_2\text{O} = 68.4 \text{ Kg. cal.}$, that of $\text{Li}_2\text{SO}_4 \text{ (anhyd.)} = 342.4 \text{ Kg. cal.}$, heat of solution of $\text{Li}_2\text{SO}_4 = 6.05 \text{ Kg. cal.}$
- 524 What weight of calcium CaH_2 is required to give, when treated with water, sufficient hydrogen to fill a Zeppelin of 500,000 cubic metres capacity under atmospheric conditions of 750 mm. and 15°C. ?
- 525 The specific heat of a metal is .031 calories per gm., and 0.3943 g. the anhydrous chloride, dissolved in water, required 30 c.c. of .970 $N/10 \text{ AgNO}_3$ to precipitate the chlorine. Calculate the atomic weight of the metal.
- 526 A sample of lead oxide was examined (a) by heating with hydrochloric acid and passing the chlorine liberated into an excess of potassium iodide solution, and titrating the iodine with decinormal sodium thiosulphate; (b) by heating and collecting the water vapour evolved. One gram of the oxide gave (a) chlorine equivalent to 24.8 c.c. thiosulphate, and (b) .01118 g. water. Suggest a formula for the oxide.
- 527 3 c.c. of a mixture of marsh gas and ethylene were exploded with excess of air. Sodium hydroxide absorbed from the residue, 5 c.c. Find the proportions of the mixture.
- 528 0.313 g. of a hydrated higher oxide of barium when dissolved in excess of dilute sulphuric acid, decolorised 20 c.c. of $N/10$ potassium permanganate. 0.4695 g. of the same oxide left on ignition 0.2295 g. of BaO . Determine the simplest molecular formula of the oxide.
- 529 15 c.c. of a certain hydrocarbon were mixed with 100 c.c. of oxygen in a eudiometer. After exploding KOH absorbed 45 c.c. of gas from the residue, the remaining 25 c.c. being oxygen. What was the formula of the hydrocarbon?
- 530 Semi-water gas is being generated in a self-contained apparatus. All the heat available from the action of the air blast on the carbon is available for generating the steam and for supplying heat absorbed in the formation of water gas from it. Assuming that the following reactions go to completion, calculate the percentage of the semi-water gas by volume:—
- $$\begin{array}{rcl} 2\text{C} + \text{O}_2 & = & 2\text{CO} + 58,000 \text{ cal.} \\ \text{H}_2\text{O} + \text{C} & = & \text{H}_2 + \text{CO} - 29,800 \text{ cal.} \end{array}$$
- The heat required to vaporise 18 g. of water = 10,800 cal.
Air contains 21% of oxygen by volume.

ANSWERS TO PROBLEMS

(Answers are given only to those problems with odd numbers.)

CHAPTER I

PROBLEMS ON THE LAWS OF CHEMICAL COMBINATION AND CHEMICAL EQUIVALENTS

- | | |
|--|----------------------|
| 1. Amounts O are as
2 : 3 : 4 : 6 : 7 | 19. 29.34 |
| 3. Si is as 6 : 8 : 9 | 21. 100.34 |
| 5. I is as 1 : 3 : 4 | 23. 29.748 |
| 7. 1.69 c.c. | 25. 30.67 |
| 9. 1095 c.c. | 27. 107.93 |
| 11. 29.41 | 29. 30.67 |
| 13. 15.87 | 31. 29.68 |
| 15. 29.37 | 33. 32.68 |
| 17. 27.92 | 35. 127.2 |

CHAPTER II

PROBLEMS ON THE CALCULATION OF PERCENTAGE COMPOSITION

37. K 19%, Sn 29%, Cl 52%
39. Ba 46.2%, S 21.5%, O 32.3%
41. C 83.4%, H 5.5%, O 11.1%
43. Na 44.2%, H 1.9%, N 53.9%
45. N 21.5%, H 6.2%, Al 13.8%, F 58.4%
47. K 22.6%, Cr 10.1%, C 13.9%, N 16.3%, S 37.1%
49. N 2.9%, H 0.8%, S 13.4%, O 26.8%, Cr 10.9%, H₂O 45.2%
51. Co 22.1%, N 31.6%, H 6.7%, Cl 39.8%
53. K 35.2%, Mn 16.6%, N 25.3%, O 4.8% C 18.1%
55. Pt 60.6%, Cl 22.0%, CO 17.4%

PROBLEMS ON THE CALCULATION OF EMPIRICAL FORMULÆ FROM PERCENTAGE COMPOSITION

- | | |
|--|---|
| 57. SF ₆ | 73. CoCl ₂ .3NH ₃ |
| 59. SrCrO ₄ | 75. HgC ₄ H ₈ O ₄ |
| 61. FeCuS ₂ ✓ | 77. BaC ₁₂ H ₁₀ S ₂ O ₆ |
| 63. H ₂ SeO ₄ | 79. NaOC ₆ H ₅ |
| 65. KClO ₄ | 81. Al ₂ O ₃ .2SiO ₂ .2H ₂ O |
| 67. CaHPO ₄ | 83. K ₂ O.2UO ₃ .V ₂ O ₅ .8H ₂ O |
| 69. Na ₂ HPO ₄ .12H ₂ O | 85. (Na,K) ₂ O.(Fe,A) ₂ O ₃ .
4SiO ₂ |
| 71. CrCl ₃ .6NH ₃ | |

PROBLEMS ON GRAVIMETRIC RELATIONSHIPS

- | | |
|---------------|------------------------|
| 87. 15.67 Kg. | 97. 12% |
| 89. 38.68% | 99. 94.8% |
| 91. 99.85% | 101. 16.33 Kg. |
| 93. 95.10% | 103. 85% |
| 95. 60% | 105. 11.1% Na, 1.1% K. |

CHAPTER III

PROBLEMS INVOLVING GAS VOLUMES AND GAS ANALYSIS

107. 2 litres
 109. 2.5 l., 10 l., 15 l., 12.5 l.
 111. (1) 750 c.c., (2) 125 c.c., (3) 300 c.c., (4) 500 c.c.
 113. 23 c.c.
 115. NH_3
 117. 164.0 c.c.
 119. 7 c.c. CH_4 , 5 c.c. C_2H_4
 121. 11.4 c.c. CO , 7.7 c.c. CH_4 , 1.3 c.c. H_2
 123. 4.86% CH_4 , 20% O_2 , 75.14% N_2
 125. C_3H_8
 127. 60% CH_4 , 40% C_2H_2
 129. 10.28%
 131. 5.49%
 133. 7.08% CO_2 , 48.33% H_2 , 44.68% CO
 135. 12.9% CO_2 , 13.2% CO , 2.3% CH_4 , 25.1% H_2 , 46.5%, N_2

PROBLEMS ON THE USE OF THE GRAM MOLECULAR VOLUME

- | | |
|--------------------------|--|
| 137. 26.43 litres | 151. 54.96 Kg. |
| 139. 89.15 l.; 18.72 l. | 153. 47.20 l. O_2 , 2.195 l. N_2 ,
39.50 l. CO_2 |
| 141. 13.07 gm.; 18.30 l. | 155. (a) 9.135 l., (b) 5.334 l. |
| 143. 467 cu.m. | 157. 1767 Kg. |
| 145. 27.33 gm. | 159. 23% Na_2CO_3 , 45% NaCl ,
32% KNO_3 |
| 147. 7.05 l.; 4.7 l. | |
| 149. 607.1 Kg. | |

PROBLEMS ON VAPOUR DENSITY AND MOLECULAR WEIGHT

- | | |
|--|---|
| 161. 2.00, 10.08, 19.97; at wts.
4.00, 20.16, 39.94 | 169. 77.4 |
| 163. 1.2506 gm. per l.; 14.007 | 171. 104.5 |
| 165. mean M.Wt. = 217; P_4O_6 | 173. NO |
| 167. 23.2 | 175. SiH_4 , Si_2H_6 , Si_3H_8 |

PROBLEMS ON THE DEGREE OF ASSOCIATION

177. 107.7
 179. 100%
 181. 1.1%, 29.1%, 68.6%, 95.8%
 183. SO_2 , density = 40; 39.6; 33.3; SO_2 , density = 32
 185. 17.75%, 18.32

PROBLEMS ON THE DIFFUSION OF GASES

187. 16.1
 189. 1.608 : 1
 191. 9.92 min.; 7.65 min.
 195. 1.877 : 1
 197. 235
 199. $\text{C}_2\text{H}_7\text{N}$
 201. 31; CH_3NH_2
 203. 192, S_8 ; 64, S_2
 205. 42% SO_3

CHAPTER IV

PROBLEMS ON ATOMIC WEIGHT DETERMINATION

207. 196.5
 209. 59.0
 211. 6.956
 213. 207.9
 215. 55.836
 217. 194.83
 219. 65.99
 221. 74.92
 223. 52.005
 225. 132.80
 227. 87.68
 229. 48.09
 231. 79.33
 233. 101.7
 235. 206.9
 237. 127.53
 239. ~~183.88~~
 241. 48.08
 243. 75.00
 245. 72.5

CHAPTER V

PROBLEMS ON ELECTROLYSIS

247. 0.991 gm. I_2 , 1.285 gm. Zn
 249. 0.482 gm.
 251. 0.4448 gm., 0.2224 gm.
 253. 0.0994 amps.
 255. 0.0003294
 257. 0.0005055

PROBLEMS ON THE CONDUCTIVITY OF ELECTROLYTES

259. 102.9
 261. 4.60
 263. 113.5
 265. .298, .394, .495, .602, .710, .805, .882, .931.

PROBLEMS ON OSMOTIC PRESSURE

267. 1.31 atmos.
 269. 62
 271. 240; 2%
 273. 84%
 275. 150

PROBLEMS ON MOLECULAR WEIGHTS FROM FREEZING POINT DEPRESSION

277. 8
 279. ~~143~~
 281. 2.68, 84%
 283. 73.4%

PROBLEMS ON MOLECULAR WEIGHT FROM THE ELEVATION OF THE BOILING POINT

285. 182
287. N_4S_4

289. 5.17

CHAPTER VI VOLUMETRIC ANALYSIS

291.	1.981 <i>N</i> , 2.547 <i>N</i>	339.	87.26%
293.	148.05, 105.75, 201.34	341.	21.1 vols.
295.	.952 <i>N</i> /10, 3.81 gm./l.	343.	29.5%
297.	.9625 <i>N</i> /10	345.	7.6 vols.
299.	73.4%	347.	29.37% ferrous, 1.22% ferric
301.	15.83 c.c.	349.	.0728 <i>N</i>
303.	18.05 c.c.	351.	39.8 c.c.
305.	25.85 c.c., 12.9 c.c.	353.	31.96%
307.	934.6 c.c.	355.	52.3%
309.	8.68%	357.	67.94%
311.	9.255 gm./l.	359.	76.49%
313.	23.9 pts. $CaCO_3$, 24.8 pts. $CaSO_4$	361.	29.23%
315.	17.22 c.c., 27.89 c.c.	363.	26.40%
317.	33.95 c.c., 45.9 c.c.	365.	27.14%
319.	4.21 gm. K_2SO_4 , 5.79 gm. $KHSO_4$	367.	4.01 gm./l.
321.	137.3	369.	1.752 pts. per 100,000
323.	120.6	371.	50.03%
325.	9.03	373.	84.1%
327.	(a) 0.0307 gm., (b) 2.47 gm./l.	375.	0.588 gm.
329.	.527 <i>N</i> /10	377.	87.6
331.	7% ferrous, 28% ferric	379.	91.41%
333.	.925 <i>N</i> /10, .00518 gm./c.c.	381.	(a) 151.8, (b) 0.42 gm./sec.
335.	97.80%	383.	60.56%
337.	75.69%	385.	12.02%
		387.	99.70%
		389.	5.62%

CHAPTER VII

PROBLEMS ON THERMOCHEMISTRY

391.	4.72 Kg.	411.	36,400 cal.
393.	-69,200 cal.	413.	69,400 cal.
395.	97,580 cal.	415.	5,400 cal.
397.	23,900 cal.	417.	105,420 cal.
399.	2,270 cal., 2,440 cal.	419.	9,290 cal.
401.	12.18 Kg.	421.	409,610 cal.
403.	192,500 cal.	423.	231,200 cal.
405.	6,980 cal., 15,950 cal., 20,380 cal., 24,080 cal.	425.	-1,500 cal.
407.	-6,000 cal.	427.	13,085 cal.
409.	22,020 cal.	429.	11,865 cal.

MISCELLANEOUS PROBLEMS

431. 20 c.c. N_2O , 11 c.c. O_2
 433. CH_3N
 435. SF_6
 437. 44.3
 439. 136
 441. 10 c.c. NO , 15 c.c. N_2
 443. 80.17 c.c.; 45.5 c.c.
 445. $CoCl_2 \cdot 4NH_3$
 447. 43.8% ZnO
 449. 9.34%
 451. 7%
 453. 96.89%
 455. F_2O
 457. .952 $N/10$
 459. 30.2% Cd ; 69.5% Hg
 461. 2.51%
 463. 53.5% $CaCO_3$; 46.5% $MgCO_3$
 465. 15,930,000 cal.
 467. -11,800 cal.
 469. 887 cu. metres
 471. $COCl_2$
 473. $FeCl_2 \cdot 6NH_3$
 475. 7,696 cu. metres
 477. 8
 479. 51.4% $NaBr$
 481. 24.3; 7
 483. 10%
 485. 23.2 d
 487. 63.46%
 491. $MgCl_2 \cdot NH_4Cl \cdot 6H_2O$
 493. 1 vol. steam : 2.9 vols. air
 495. 489 cu. metres
 497. 6,089 cu. metres
 499. 26 kg. cal. per gm. atom Ag
 501. 73.22 gm.
 503. 12 c.c. NO , 14 c.c. N_2O , 9 c.c. N_2
 505. 20.5% O_2
 507. 4.08 g./litre; 354.6 c.c.
 509. 225.6.
 511. 53.86 c.c.
 513. 92.32%.
 515. C_4H_{10}
 517. Sodium hyponitrite, $Na_2N_2O_2$; 78.26%.
 519. 10.76%.
 521. 4 c.c. C_2H_6 .
 523. 15.8 Kg. cal.
 525. 200.0.
 527. 1 c.c. CH_4 .
 529. C_3H_8 .

TABLE I
TENSION OF WATER VAPOUR.

Temperature °C.	Pressure mm.	Temperature °C.	Pressure mm.
0	4.6	16	13.5
1	4.9	17	14.4
2	5.3	18	15.3
3	5.7	19	16.3
4	6.1	20	17.4
5	6.5	21	18.5
6	7.0	22	19.6
7	7.5	23	20.9
8	8.0	24	22.1
9	8.5	25	23.5
10	9.1	26	25.0
11	9.8	27	26.5
12	10.4	28	28.1
13	11.1	29	29.7
14	11.9	30	31.5
15	12.7		

- TABLE II

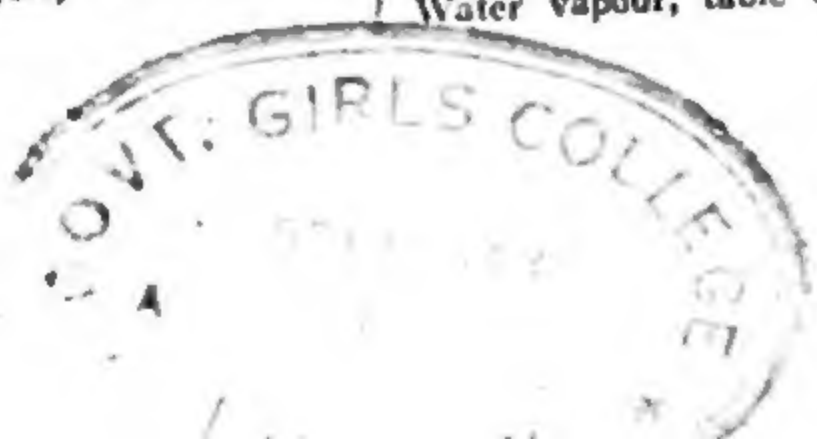
ATOMIC WEIGHTS

ELEMENT	SYMBOL	ATOMIC WEIGHT	ELEMENT	SYMBOL	ATOMIC WEIGHT
Aluminium	Al	26.97	Neodymium	Nd	144.27
Antimony	Sb	121.76	Neon	Ne	20.183
Argon	A	39.944	Nickel	Ni	58.69
Arsenic	As	74.93	Niobium	Nb	
Barium	Ba	137.36	(Columbium)	(Cb)	92.91
Beryllium	Be	9.02	Nitrogen	N	14.008
Bismuth	Bi	209.00	Osmium	Os	191.5
Boron	B	10.82	Oxygen	O	16.0000
Bromine	Br	79.916	Palladium	Pd	106.7
Cadmium	Cd	112.41	Phosphorus	P	31.02
Cæsium	Cs	132.91	Platinum	Pt	195.23
Calcium	Ca	40.08	Potassium	K	39.10
Carbon	C	12.00	Praseodymium	Pr	140.92
Cerium	Ce	140.13	Radium	Ra	225.97
Chlorine	Cl	35.457	Radon	Rn	222
Chromium	Cr	52.01	Rhenium	Re	186.31
Cobalt	Co	58.94	Rhodium	Rh	102.91
Copper	Cu	63.57	Rubidium	Rb	85.44
Dysprosium	Dy	162.46	Ruthenium	Ru	101.7
Erbium	Er	167.64	Samarium	Sm	150.43
Europium	Eu	152.0	Scandium	Sc	45.10
Fluorine	F	19.00	Selenium	Se	78.96
Gadolinium	Gd	157.3	Silicon	Si	28.06
Gallium	Ga	69.72	Silver	Ag	107.880
Germanium	Ge	72.60	Sodium	Na	22.997
Gold	Au	197.2	Strontium	Sr	87.63
Hafnium	Hf	178.6	Sulphur	S	32.06
Helium	He	4.002	Tantalum	Ta	181.4
Holmium	Ho	163.5	Tellurium	Te	127.61
Hydrogen	H	1.0078	Terbium	Tb	159.2
Indium	In	114.76	Thallium	Tl	204.39
Iodine	I	126.92	Thorium	Th	232.12
Iridium	Ir	193.1	Thulium	Tm	169.4
Iron	Fe	55.84	Tin	Sn	118.70
Krypton	Kr	83.7	Titanium	Ti	47.90
Lanthanum	La	138.92	Tungsten	W	184.0
Lead	Pb	207.22	Uranium	U	238.14
Lithium	Li	6.940	Vanadium	V	50.95
Lutecium	Lu	175.0	Xenon	Xe	131.3
Magnesium	Mg	24.32	Ytterbium	Yb	173.04
Manganese	Mn	54.93	Yttrium	Y	88.92
Mercury	Hg	200.61	Zinc	Zn	65.38
Molybdenum	Mo	96.0	Zirconium	Zr	91.22

INDEX

- Abnormal vapour densities, 63
- Accurate determination of atomic weights, 83
- Acid-alkali titrations, 116
- Analysis by means of oxidising agents, 124
- Answers to problems, 175
- Association, degree of, 104
- Atomic structure of matter, 20
- Atomic theory, the, 20
- Atomic theory, the difficulties of, 22
- Atomic weight, accurate determination of, 83
- Atomic weight, determination of, 74, *et seq.*
- Atomic weight determinations, problems on, 85
- Atomic weight, equivalent and valency, 73
- Atomic weights, table of, 180
- Avogadro's hypothesis, 40
- Boyle's Law, 12
- Calculations involving the volumes of gases, 41
- Cannizzaro's method of atomic weight determination, 74
- Charles' Law, 13
- Chemical equations, 91
- Chemical equivalents, 10
- Chemical equivalents, problems on, 17
- Combined gas law, the, 12
- Combining proportions, law of, 10
- Conductivity of electrolytes, 95
- Conductivity of electrolytes, problems on, 98
- Conservation of mass, 1
- Conservation of mass, Landolt's experiments on, 5
- Constant proportions, law of, 7
- Criteria of isomorphism, 80
- Dalton's Law, 14
- Degree of dissociation, 65
- Degree of dissociation, problems on, 66
- Density of gases, 53
- Determination of carbonates, 120
- Determination of copper, 130
- Determination of equivalents, 11
- Determination of hydrogen peroxide, 127
- Determination of molecular weights, 49, 101, 103
- Difficulties of the atomic theory, 22
- Diffusion of gases, 67
- Diffusion of gases, problems on, 70
- Dissociation, degree of, 65, 104
- Dulong and Petit's Rule, 76
- Dumas' method for the determination of vapour densities, 56
- Electrolysis, 90
- Electrolysis, problems on, 94
- Electrolytes, conductivity of, 95
- Empirical formulæ, calculation of, 27
- Empirical formulæ, problems on, 30
- Equations, chemical, 31
- Equivalent proportions, law of, 10
- Equivalent weights of compounds, 110
- Equivalents, 1, 10
- Equivalents, determination of, 11
- Equivalents, determination of by volumetric analysis, 123
- Endothermic reactions, 149
- Exothermic reactions, 149
- Faraday's Laws of electrolysis, 91
- Formulæ, 25
- Formulæ of gases, determination of, 60
- Formulæ of minerals, 29
- Freezing point depression, 103
- Gas analysis calculations, 42
- Gas densities, 53
- Gas law, the combined, 12
- Gram molecular volume, problems involving the, 51
- Gravimetric analysis, 33
- Gravimetric relationships, problems on, 35
- Heat of reaction, 149
- Heats of reaction, indirect determination of, 157
- Heats of formation, indirect determination of, 155
- Hess, law of, 154
- Hoffmann's method of determining vapour density, 55
- Indicators, 115
- Interrelation of the atomic weights, 84
- Intrinsic energy, 151
- Iodine titrations, 129
- Ionic hypothesis, the, 93
- Isomorphism, 78
- Isotonic solutions, 101
- Landolt's work on conservation of mass, 5
- Law of combining proportions, 10

- Law of constant proportions, 7
 Law of equivalent proportions, 10
 Law of gas volumes, 38
 Law of Hess, 154
 Law of isomorphism, 78
 Law of multiple proportions, 9
 Laws of combination, 1
 Laws of combination, problems on, 17
 Laws of combination and the atomic theory, 21
 Litmus, 116
 Methyl orange, 116
 Methyl red, 116
 Miscellaneous problems, 164
 Mitscherlich's law of isomorphism, 78
 Modern theory of the structure of matter, 23
 Molecular weight and the volume of gases, 49
 Molecular weights from boiling point elevation, 107
 Molecular weights from boiling point elevation, problems on, 108
 Molecular weights from freezing point depression, 103
 Molecular weights from freezing point depression, problems on, 106
 Molecular weights from osmotic pressure, 101
 Molecular weights from vapour densities, 49
 Molecular weights from vapour densities, problems on, 61
 Morley's complete synthesis of water, 4
 Multiple proportions, law of, 9
 Neutralisation, 115
 Normal solutions, 112
 Normal solutions of oxidising agents, 125
 Osmotic pressure, 99
 Osmotic pressure, problems on, 103
 Oxidising agents, normal solutions of, 125
 Partial pressure, 14
 Percentage composition, 26
 Phenolphthalein, 116
 Physical heat effects, 152
 Precipitation analysis, 131
 Problems, miscellaneous, 164
 Problems on atomic weight determinations, 85
 Problems on boiling point elevation, 108
 Problems on the conductivity of electrolytes, 98
 Problems on the degree of dissociation, 66
 Problems on diffusion of gases, 70
 Problems on electrolysis, 94
 Problems on empirical formulae from percentage composition, 30
 Problems on equivalents, 17
 Problems on freezing point depression, 106
 Problems on gas analysis, 45
 Problems on gas volumes, 45
 Problems on gram molecular volume, 51
 Problems on gravimetric relationships, 35
 Problems on laws of combination, 16
 Problems on molecular weights, 61
 Problems on osmotic pressure, 103
 Problems on percentage composition, 27
 Problems on reduction of gas volumes, 17
 Problems on thermochemistry, 159
 Problems on vapour densities, 51
 Problems on volumetric analysis, 137
 Reduction of gas volumes, 13
 Reduction of gas volumes, problems on, 17
 Relations between molecular weight and volume, 49
 Rule of Dulong and Petit, 76
 Sodium thiosulphate, standardisation of, 129
 Standardisation of solutions, 117
 Stas' work, 2
 Structure of matter, modern theory of, 23
 Table of atomic weights, 180
 Table of tension of water vapour, 179
 Thermochemistry, 149, *et seq.*
 Thermochemistry, problems on, 159
 Titrations, acid-alkali, 116
 Titrations, dichromate, 125
 Titrations, iodine, 129
 Titrations, permanganate, 125
 Titrations, silver, 131
 Titrations, two indicator, 120
 Two indicator titrations, 120
 Vapour densities, abnormal, 63
 Vapour density determinations, 55
 Vapour density determinations, Dumas' method, 56
 Vapour density determinations, Hoffmann's method, 55
 Vapour density determinations, problems on, 61
 Vapour density, determinations, Victor Meyer's method, 58
 Volhard's method of silver estimation, 133
 Volumetric analysis, 110 *et seq.*
 Volumetric analysis, miscellaneous calculations on, 134
 Volumetric analysis, problems on, 137
 Water vapour, table of tension of, 179



Mufti. Muqbool Ahamed

Penname: Keats and.

Govt. College for Women,

SRINAGAR

123 456 789

SRIN																			
	1012	1014	1016	1019	1021	001	111	222											
01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	001	111	222						
02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	001	111	222						
03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	001	111	222						
04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	011	112	222						
05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	011	112	222						
06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	011	112	222						
07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	011	112	222						
08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	011	112	223						
09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	011	112	223						
10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	011	112	223						
11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	011	122	223						
12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	011	122	223						
13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	011	122	233						
14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	011	122	233						
15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	011	122	233						
16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	011	122	233						
17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	011	122	233						
18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	011	122	233						
19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	011	122	333						
20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	011	122	333						
21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	011	222	333						
22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	011	222	333						
23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	011	222	334						
24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	011	222	334						
25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	011	222	334						
26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	011	223	334						
27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	011	223	334						
28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	011	223	344						
29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	011	223	344						
30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	011	223	344						
31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	011	223	344						
32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	011	223	344						
33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	011	223	344						
34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	112	233	445						
35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	112	233	445						
36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	112	233	445						
37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	112	233	445						
38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	112	233	445						
39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	112	233	455						
40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	112	234	455						
41	2570	2576	2582	2588	2599	2600	2606	2612	2618	2624	112	234	456						
42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	112	234	456						
43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	112	334	456						
44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	112	334	456						
45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	112	334	556						
46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	112	334	556						
47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	112	334	556						
48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	112	344	566						
49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	112	344	566						
	0	1	2	3	4	5	6	7	8	9	123	456	789						

ANTILOGARITHMS

Log.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	9
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7		
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6			
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6			
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6			
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6			
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6			
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	6			
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	5	6			
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	4	5	6			
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	3	4	5	6			
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	3	4	5	6			
.72	5248	5260	5272	5284	5297	5309	5321	5333	5345	5357	1	2	3	4	5	6			
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5482	1	2	3	4	5	6			
.74	5495	5508	5521	5534	5546	5559	5572	5584	5597	5609	1	2	3	4	5	6			
.75	5623	5636	5649	5662	5675	5689	5702	5714	5727	5739	1	2	3	4	5	6			
.76	5754	5768	5781	5794	5808	5821	5834	5847	5860	5873	1	2	3	4	5	6			
.77	5888	5902	5916	5929	5943	5957	5970	5983	5996	6009	1	2	3	4	5	6			
.78	6026	6039	6053	6067	6081	6094	6107	6120	6133	6146	1	2	3	4	5	6			
.79	6166	6180	6194	6209	6223	6236	6250	6263	6276	6289	1	2	3	4	5	6			
.80	6310	6324	6339	6353	6367	6381	6395	6408	6422	6436	1	2	3	4	5	6			
.81	6457	6471	6486	6501	6515	6529	6543	6557	6571	6585	1	2	3	4	5	6			
.82	6607	6622	6637	6653	6667	6681	6695	6709	6723	6737	1	2	3	4	5	6			
.83	6761	6776	6792	6807	6821	6835	6849	6863	6877	6891	1	2	3	4	5	6			
.84	6918	6934	6950	6965	6980	6995	7010	7025	7040	7055	1	2	3	4	5	6			
.85	7079	7096	7112	7128	7144	7160	7176	7192	7208	7224	1	2	3	4	5	6			
.86	7244	7261	7278	7294	7311	7327	7344	7360	7377	7393	1	2	3	4	5	6			
.87	7413	7430	7447	7464	7481	7498	7515	7532	7549	7566	1	2	3	4	5	6			
.88	7586	7603	7620	7637	7654	7671	7688	7705	7722	7739	1	2	3	4	5	6			
.89	7760	7777	7794	7811	7828	7845	7862	7879	7896	7913	1	2	3	4	5	6			
.90	7930	7947	7964	7981	8000	8017	8034	8051	8068	8085	1	2	3	4	5	6			
.91	8103	8120	8137	8154	8171	8188	8205	8222	8239	8256	1	2	3	4	5	6			
.92	8273	8290	8307	8324	8341	8358	8375	8392	8409	8426	1	2	3	4	5	6			
.93	8443	8460	8477	8494	8511	8528	8545	8562	8579	8596	1	2	3	4	5	6			
.94	8613	8630	8647	8664	8681	8698	8715	8732	8749	8766	1	2	3	4	5	6			
.95	8783	8800	8817	8834	8851	8868	8885	8902	8919	8936	1	2	3	4	5	6			
.96	8953	8970	8987	9004	9021	9038	9055	9072	9089	9106	1	2	3	4	5	6			
.97	9123	9140	9157	9174	9191	9208	9225	9242	9259	9276	1	2	3	4	5	6			
.98	9293	9310	9327	9344	9361	9378	9395	9412	9429	9446	1	2	3	4	5	6			
.99	9463	9480	9497	9514	9531	9548	9565	9582	9599	9616	1	2	3	4	5	6			
1.00	9633	9650	9667	9684	9701	9718	9735	9752	9769	9786	1	2	3	4	5	6			

GOVT. COLLEGE
FOR WOMEN LIBRARY
SRINAGAR.

Members of College Teaching Staff can borrow ten books at a time and can retain these for one month.
A student of the college can borrow one book at a time, and can retain it for 14 days.
Books in any way injured or lost shall be paid for or replaced by the borrower.

1	2	3	4	5	6	7	8	9
---	---	---	---	---	---	---	---	---